

THE STATE OF NEW HAMPSHIRE

BELKNAP, SS.

SUPERIOR COURT

Forrester Environmental Services, Inc.

78 Tracy Way
Meredith, NH 03253
and
Keith E. Forrester
78 Tracy Way
Meredith, NH 03253

v.

Wheelabrator Technologies, Inc.

4 Liberty Lane
Hampton, NH 03842

Docket No. 10-E-0023

AMENDED PETITION FOR DAMAGES AND INJUNCTIVE RELIEF

Plaintiff Forrester Environmental Services, Inc. ("FESI") and Keith E. Forrester ("Forrester"), as and for their Amended Petition against Defendant Wheelabrator Technologies, Inc. ("WTI"), allege as follows:

NATURE OF THE ACTION

1. This is a civil action for recovery of damages and injunctive relief, arising from WTI's tortious interference with FESI's contractual relations and prospective advantage, misappropriation of Forrester's commercially valuable methods, as more fully set forth herein, and violation of NH RSA 358-A:2.

PARTIES AND JURISDICTION

2. Plaintiff FESI is a New Hampshire corporation with its principal place of business at 78 Tracy Way, Meredith, New Hampshire 03253.

3. Plaintiff Forrester is an individual residing at 78 Tracy Way, Meredith, New Hampshire 03253.

4. On information and belief, defendant, Wheelabrator Technologies, Inc. ("WTI") has its principal place of business at 4 Liberty Lane, Hampton, New Hampshire 03842.

JURISDICTION AND VENUE

5. On information and belief, this Court has personal jurisdiction over Defendant WTI, in that WTI has its principal place of business in the State of New Hampshire, and conducts business in the State of New Hampshire.

6. Venue is proper based on the domicile/business addresses of the parties.

FACTS COMMON TO ALL COUNTS

7. Keith E. Forrester ("Forrester") is the President of FESI, which he founded in 1992. From 1985 to 1992, Forrester worked for Wheelabrator Environmental Systems, Inc. ("WES"), WTI's predecessor, as Senior Environmental Engineer. While at WES, Forrester invented certain technology for the use of water-soluble phosphates to immobilize lead in bottom ash and shredder residues. Said technology was the subject of two United States Patents, of which Forrester was the inventor and which he assigned to WES, U.S. Patents No. 5,245,114 ("the '114 Patent) and 5,430,233 ("the '233 Patent").

8. Forrester left WES in 1992 after complaining to WES's management about actions taken by WES which Forrester viewed as unethical, and after writing a report to WES's management detailing various acts of wrongdoing, which WES's management destroyed.

9. Since 1992, WES/WTI has engaged in numerous actions to interfere with FESI's business and harm Forrester, including infringing on patents held by Forrester and lying to

FESI's customers, which conduct for many years FESI and Forrester had to endure because they lacked the resources to litigate.

10. WTI and FESI are direct competitors in that both provide technology (chemical treatment) for the treatment of lead and other hazardous (toxic) metals found in incinerator ash, auto shredder residue, and copper wire insulation residue.

11. Both FESI and WTI have clients worldwide.

12. While at WES, Forrester oversaw contractors who were the inventors of certain technology for immobilization of lead and cadmium in incinerator ash which is the subject of a United States Patent assigned by them to WES, U.S. Patent No. 4,737,356 ("the "356 Patent"), which is now in the public domain since the patent term ended in 2008.

13. The '356, '114, and '233 Patents are expressly limited to the use of water soluble phosphates, which term is specifically defined therein to mean and require water solubility of at least to the extent of about 5 grams per 100 milliliters.

14. WTI does not own any patents covering the use of water insoluble phosphates for the treatment of lead in bottom ash, flyash or combined ash, auto shredder residue, or copper wire insulating residue, including but not limited to the use of calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, granular triple superphosphate or dicalcium phosphate dihydrate powder.

15. WTI sells a stabilization process under the name "WES-PHix®." The WES-PHix® process uses a form of water soluble phosphate to reduce the solubility of certain heavy metals in solid incinerator ash and shredder waste by altering the chemical composition of the waste. Forrester is the inventor of WES-PHix®, covering treatment of incinerator bottom ash and auto and wire shredder waste.

16. WES-PHix® requires the treatment of ash or shredder waste using water soluble phosphate, especially phosphoric acid. WES-PHix® does not include the use of water insoluble phosphates, including but not limited to calcium phosphates, monocalcium phosphates, dicalcium phosphates, tricalcium phosphates, granular triple superphosphate and dicalcium phosphate dihydrate powder. Dicalcium phosphate dihydrate powder ("DCPDHP") is water insoluble with a water solubility of 0.02 gr/100 ml, and does not constitute a water soluble phosphate under the definition used for that term in WTI's '356, '114 and '233 Patents.

17. On information and belief, on or about February 19, 2001, WTI, through its agent and licensee Bio Max Environmental, granted a sublicense to Kuo-Bin Ceramic Ind. Co., Ltd of Taipei, Taiwan, also known as Kobil Environmental Enterprises Co., Ltd. ("Kobil") for the use of WES-PHix® to treat incinerator bottom ash at Kobil's Taipei facility.

18. The use of WES-PHix® phosphoric acid for stabilization of bottom ash caused a strong odor problem and, about 1% of the time, resulted in failure of the Toxicity Characteristic Leaching Procedure (TCLP) standard for lead at the Kobil plant.

19. In or around 2004, TYT (USA) learned that Kobil was searching for an alternative to their WES-PHix Bottom Ash Stabilization System due to odor and TCLP problems. In response, TYT advised Kobil that Forrester-FESI was available to assist. Consequently, Kobil approached Forrester, as inventor of the WTI Bottom Ash WES-PHix® and the '114 and '233 Patents, and asked him to solve certain problems that had occurred when Kobil used WES-PHix® to treat bottom ash. Kobil informed Forrester that neighbors and the Taiwan Environmental Protection Agency in Taipei had complained to Kobil about odor caused by the use of WES-PHix® and also that WES-PHix® had failed to pass the applicable TCLP tests on some occasions.

20. On January 19, 1999, United States Letters Patent No. 5,860,908, entitled "Water insoluble heavy metal stabilization process" ("the '908 Patent"), was issued to Plaintiff Forrester, for an invention in a method of immobilizing heavy metal in a free flowing dry or wet waste or heavy metal contaminated material which maintains its free flowing nature after immobilizing treatment. A copy of the '908 Patent is attached hereto as Exhibit 1. Forrester owned the '908 Patent throughout the period of the Defendant WTI's infringing acts and still owns the patent. Forrester invented the invention claimed in the '908 Patent after leaving WES and forming FESI.

21. On April 18, 2000, United States Letters Patent No. 6,050,929, entitled "Method for stabilizing heavy metal bearing waste in a waste generation stream" ("the '929 Patent"), was issued to Plaintiff Forrester, for an invention in a method for stabilizing a heavy metal in a heavy metal containing material (including, but not limited to, insulation wire waste and autoshredder waste) to reduce leaching of the heavy metal therefrom when said material is exposed to natural or induced leaching conditions. A copy of the '929 Patent is attached hereto as Exhibit 2. Forrester owned the '929 Patent throughout the period of the Defendant WTI's infringing acts and still owns the patent. Forrester invented the invention claimed in the '929 Patent after leaving WES and forming FESI.

22. On August 12, 2005, Forrester filed a Taiwan patent application, entitled "Method for Stabilization of Slag, Matte and Bottom Ash," which incorporates and teaches the use of calcium phosphates, monocalcium phosphates, dicalcium phosphates, granular triple superphosphate ("GTSP") and tricalcium phosphates as TCLP Pb stabilizers for incinerator bottom ash. The application was assigned Application No. 094127495, and was published in the Taiwan Patent Office on or about June 1, 2006, Publication No. 200616722.

23. On August 28, 2007, Forrester filed a Taiwan patent application, entitled "Method for Stabilization of Heavy Metals and Odor Control with Dicalcium Phosphate Dihydrate Powder," which incorporates and teaches the use of DCPDHP as a TCLP Pb and odor control agent for Kobil incinerator bottom ash. The application was assigned Application No. 096131793, and was published in the Taiwan Patent Office on or about January 1, 2009, Publication No. 200900170.

24. FESI sells chemicals and provides stabilization processes that were patented under the '908 and '929 Patents under the name "FESI BOND® DRY."

25. When he was approached by Kobil, Forrester offered to develop a chemical covered by his '908 and '929 Patents and/or develop a new BA stabilization technology that would solve the problems with WES-PHix® that had been identified by Kobil.

26. On August 27, 2004, FESI entered into a "Stabilization Chemical Supply Agreement" ("Agreement") with Kobil to provide FESI-BOND® DRY stabilization chemicals for the purpose of stabilizing incinerator bottom ash. As part of the Agreement Appendix, FESI disclosed to Kobil the use of water insoluble dry stabilizers including calcium phosphate, monocalcium phosphate, GTSP, dicalcium phosphate and tricalcium phosphate.

27. Taiwan is the only country in the world that permits separate stabilization and commercial product reuse of incinerator bottom ash.

28. FESI's Agreement with Kobil includes all bottom ash stabilization projects in Taiwan including the Kobil facility, where bottom ash is separated from incinerator flyash, and where bottom ash requires stabilization prior to reuse as construction aggregate.

29. In 2004 and 2005, as the result of pioneer research at FESI LABS in order to produce a dry stabilizer capable of stabilizing Bottom Ash TCLP Pb while reducing odor as

compared to WES-PHix® phosphoric acid stabilization, Forrester invented a chemical called FESI-BOND® DCPDHP employing dicalcium phosphate dihydrate powder specifically engineered for use by Kobil at its Taiwan facility, and located and modified a source for said chemical in Shanghai, China.

30. Kobil constitutes the entire market for FESI-BOND® DCPDHP.

31. On information and belief, WTI gained actual knowledge of the Agreement and of FESI's contractual relations with Kobil in or around 2005.

32. FESI-BOND® DRY stabilization chemicals includes but is not limited to calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and dicalcium phosphate dihydrate in powder form. DCPDHP is water insoluble and is applied in a dry treatment process.

33. FESI-BOND® DRY water insoluble chemicals, including calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and/or FESI-BOND® DCPDHP, are not covered by any of WTI's patents and are not included in WTI's WES-PHix® system.

34. The Taiwan Environmental Protection Agency approved the use of FESI-BOND® DCPDHP by Kobil for Bottom Ash TCLP stabilization with low stabilization process generated odor production in 2005.

35. Kobil commenced purchases of FESI-BOND® DCPDHP from FESI on or about April 29, 2005, and made regular purchases thereafter in the amount of approximately \$60,000 per month.

36. In or around June, 2007, WTI approached Kobil and knowingly and intentionally made false statements to Kobil regarding Forrester, Forrester patents pending and FESI and

regarding WTI's own patents and products, including (a) statements guaranteeing that calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and DCPDHP were covered by WTI's patents, including the '114 Patent, and were within the WES-PHix® process; (b) statements that FESI had been sued by WTI in the United States and had lost the suit; and (c) written statements that Forrester had no rights to calcium phosphate use as a TCLP Pb stabilizer in Taiwan.

37. WTI made such false statements to Kobin as part of the promotion of its own business for the purpose of interfering with FESI's and Forrester's actual and prospective contractual relations with Kobin and causing Kobin to breach the Agreement with FESI and not to make royalty payments to Forrester.

38. On information and belief, WTI's decision to make such false statements and to interfere with FESI's Agreement with Kobin and Forrester's right to royalties from Kobin was made at WTI's corporate headquarters in New Hampshire.

39. In or around June, 2007, WTI explicitly required Kobin to terminate the FESI-Kobin Agreement and also required Kobin to stop all purchases and sales of FESI-BOND in Taiwan, as part of the terms and conditions of a new Kobin 2007 WES-PHix license agreement.

40. In or around June, 2007, in reliance on and by reason of WTI's requirements and false statements as above alleged, Kobin terminated the Agreement between Kobin and FESI, elected not to pay Forrester any royalty for the calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and/or DCPDHP stabilization and odor control agent invention, and entered into a new WES-PHix® license agreement with WTI ("Second WTI Agreement").

41. On information and belief, during negotiation of the Second WTI Agreement, Kobin asked WTI if WES-PHix® covered the use of dry water insoluble phosphate chemicals, and WTI falsely stated that it has a patent covering the use of "any solid, liquid or chemical form of phosphate and/or lime" including the use of dry chemicals. On information and belief, WTI made such false statements to Kobin as part of the promotion of its own business for the purpose of interfering with FESI's actual and prospective contractual relations with FESI. On information and belief, WTI's decision to make such false statements and to interfere with FESI's contract with Kobin was made at WTI's corporate headquarters in New Hampshire.

42. In or about June or July, 2007, FESI and Kobin planned to meet in Meredith, New Hampshire, for the purpose of signing a new FESI/Kobin agreement for future supply of DCPDHP to Kobin and for royalty payments to Forrester. In or about June, 2007, prior to the anticipated meeting with FESI, Kobin met with WTI in Hampton, New Hampshire. Upon information and belief, at said meeting, WTI stated to Kobin that WTI patents and WES PHix® technology covered DCPDHP provided to Kobin by FESI and the Forrester invention, and that FESI had lost a lawsuit against WTI. Thereafter, Kobin cancelled its planned meeting with FESI in New Hampshire.

43. The Second WTI Agreement falsely states that WES-PHix® patents cover "using any solid, liquid, or chemical form of phosphate and/or lime" for immobilization of metals such as lead and cadmium in solid residues.

44. Kobin terminated its business with FESI by reason of WTI's false statements and representations as above alleged and by reason of WTI's explicit requirements that FESI-Kobin Agreement be terminated and that Kobin stop all purchases and sales of FESI-BOND in Taiwan.

45. Said termination has caused, and continues to cause, both loss of revenue and irreparable harm to FESI and Forrester.

46. On information and belief, Kobin is directly purchasing calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and/or DCPDHP from sources other than FESI, and is paying WTI or its agent royalties of approximately \$1.5 million annually in connection with Kobin's purchases of calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP, and/or DCPDHP pursuant to the Second WTI Agreement; and Kobin has paid WTI or its agents royalties of approximately \$1.5 million annually in connection with Kobin's purchases of DCPDHP from FESI from April 29, 2005 to December 31, 2008, on the claims by WTI that DCPDHP was covered under WTI's patents.

47. On information and belief, WTI deliberately, willfully and intentionally made literally false statements to Kobin that: (a) calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and DCPDHP were covered by WTI's patents, including the '114 Patent, and were within the WES-PHix® process; and (b) WTI has a patent covering the use of "any solid, liquid or chemical form of phosphate and/or lime" including the use of dry chemicals.

48. On information and belief, WTI has deliberately, willfully and intentionally made literally false statements in the United States, in the course of its regular business, that: (a) calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and DCPDHP were covered by WTI's patents, including the '114 Patent, and were within the WES-PHix® process; and (b) WTI has a patent covering the use of "any solid, liquid or chemical form of phosphate and/or lime" including the use of dry chemicals.

49. On information and belief, whether calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and DCPDHP were covered by WTI's patents, including the '114 Patent, and were within the WES-PHix® process, and whether WTI has a patent covering the use of "any solid, liquid or chemical form of phosphate and/or lime" including the use of dry chemicals, all were material to Kobil's decision to breach the Agreement with FESI and Forrester and enter into the Second WTI Agreement with WTI.

50. On information and belief, whether calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and DCPDHP are covered by WTI's patents, including the '114 Patent, and are within the WES-PHix® process, and whether WTI has a patent covering the use of "any solid, liquid or chemical form of phosphate and/or lime" including the use of dry chemicals, all are material to a relevant consumer's decision to purchase a system or technology for immobilizing heavy metals in waste.

51. On information and belief, relevant consumers have been deceived or are likely to be deceived by WTI's deliberate, willful and intentional false statements concerning whether: (a) calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, GTSP and DCPDHP are covered by WTI's patents, including the '114 Patent, and are within the WES-PHix® process; and (b) WTI has a patent covering the use of "any solid, liquid or chemical form of phosphate and/or lime" including the use of dry chemicals.

COUNT I
VIOLATION OF N.H. RSA 358-A

52. Plaintiffs repeat and re-allege the allegations set forth in Paragraphs 1-51 of this Petition, as though fully set forth herein.

53. This claim arises under the Laws of the State of New Hampshire, RSA 358-A:2.

54. WTI is engaged in trade and commerce within the meaning of RSA 358-A:1.

55. The actions of WTI as above alleged constitute unfair methods of competition or unfair or deceptive acts or practices in violation of RSA 358-A:2.

56. Said acts or practices of WTI constitute a willful or knowing violation of RSA 358-A.

57. As a result of the actions of WTI as above alleged, Plaintiffs have suffered damages.

COUNT II
TORTIOUS INTERFERENCE WITH CONTRACTUAL RELATIONSHIP

58. Plaintiffs repeat and re-allege the allegations set forth in Paragraphs 1-57 of this Petition, as though fully set forth herein.

59. This claim arises under the common law of the State of New Hampshire.

60. FESI had a contractual relationship with Kobin.

61. WTI had actual knowledge of FESI's contractual relationship with Kobin.

62. By its acts as above alleged, WTI intentionally and wrongfully interfered with FESI's contractual relationship with Kobin and Forrester's prospective royalty license with Kobin.

63. The conduct of WTI as above alleged is the result of an improper motive on behalf of WTI.

64. By its acts as above alleged, WTI tortiously interfered with the business relationship between FESI and Kobin and Forrester and Kobin.

65. As a result of the actions of WTI as above alleged, FESI and Forrester have suffered damages.

COUNT III

**TORTIOUS INTERFERENCE WITH FESI'S AND FORRESTER'S
PROSPECTIVE ADVANTAGE**

66. Plaintiffs repeat and re-allege the allegations set forth in Paragraphs 1-65 of this Petition, as though fully set forth herein.

67. This claim arises under the common law of the State of New Hampshire.

68. FESI and Forrester possessed a business relationship or expectancy with Kobil, with a reasonable probability of future economic benefit.

69. WTI had actual knowledge of FESI's and Forrester's business relationship with Kobil and of FESI's and Forrester's expectancy of future economic benefit.

70. Except for the conduct of WTI as above alleged, FESI and Forrester would have continued their business relationship and entered into an expanded business relationship with Kobil.

71. WTI intentionally interfered with FESI's and Forrester's prospective economic relationship with Kobil.

72. WTI, without privilege to do so, induced or otherwise purposely caused Kobil not to enter into or continue a business relation with FESI and Forrester.

73. FESI has suffered and continues to suffer economic damage as a result of WTI's wrongful interference.

COUNT IV

MISAPPROPRIATION OF PROPRIETARY METHOD

74. Plaintiffs repeat and re-allege the allegations set forth in Paragraphs 1-73 of this Petition, as though fully set forth herein.

75. This claim arises under the common law of the State of New Hampshire.

76. On information and belief, WTI has sold and/or licensed to Kobin, in Taiwan, a method for immobilizing heavy metal in a free flowing dry or wet waste (including incinerator combined ash, flyash, bottom ash, auto shredder residue and copper wire shredder residue) including contacting the waste with a water insoluble immobilizing agent consisting of calcium phosphate, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, DCPDHP, granular triple superphosphate ("GTSP"), or triple superphosphate, that embodies the invention of the '908 Patent.

77. Kobin's practice of the method described in the above Paragraph would constitute infringement of the '908 Patent, if it occurred within the United States.

78. Kobin's extraterritorial practice of the patented method is not protected by U.S. Patent Law, or by traditional common law theories of unfair competition.

79. By its acts as above alleged, WTI misappropriated, at little or no cost, Forrester's commercially valuable method, as claimed in the '908 Patent.

80. On information and belief, WTI has sold and/or licensed to Kobin, in Taiwan, a method for stabilizing heavy metal containing material in incinerator combined ash, auto shredder residue and copper wire shredder residue employing the contacting of said heavy metal containing material with stabilizers including monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, DCPDHP, GTSP, triple super phosphate or calcium phosphate while processing said material through waste stream equipment prior to the generation of waste, that embodies the invention of the '929 Patent.

81. Kobin's practice of the method described in the above Paragraph would constitute infringement of the '929 Patent, if it occurred within the United States.

82. Kobin's extraterritorial practice of the patented method is not protected by U.S. Patent Law, or by traditional common law theories of unfair competition.

83. By its acts as above alleged, WTI misappropriated, at little or no cost, Forrester's commercially valuable method, as claimed in the '929 Patent.

84. On July 16, 1996, United States Letters Patent No. 5,536,899, entitled "Stabilization of lead bearing waste" ("the '899 Patent"), were issued to Plaintiff Forrester, for an invention in a method for reducing the leaching of lead from a lead bearing waste. A copy of the '899 Patent is attached hereto as Exhibit 3. Forrester owned the '899 Patent throughout the period of the Defendant WTI's infringing acts and still owns the patent.

85. On March 3, 1998, United States Letters Patent No. 5,722,928, entitled "Stabilization of lead bearing waste" ("the '928 Patent"), were issued to Plaintiff Forrester, for an invention in a method for reducing the leaching of lead from a lead bearing waste. The '928 Patent is a continuation-in-part of the '899 Patent. A copy of the '928 Patent is attached hereto as Exhibit 4. Forrester owned the '928 Patent throughout the period of the Defendant WTI's infringing acts and still owns the patent.

86. On December 8, 1998, United States Letters Patent No. 5,846,178, entitled "Stabilization of lead bearing waste" ("the '178 Patent"), were issued to Plaintiff Forrester, for an invention in a method for reducing the leaching of lead from a lead bearing waste. The '178 Patent is a continuation of the '928 Patent. A copy of the '178 Patent is attached hereto as Exhibit 5. Forrester owned the '178 Patent throughout the period of the Defendant WTI's infringing acts and still owns the patent.

87. On May 12, 2009, United States Letters Patent No. 7,530,939, entitled "Method for Stabilization of Heavy Metals in Incinerator Bottom Ash and Odor Control with DiCalcium

Phosphate Dihydrate Powder" ("the '939 Patent"), were issued to Plaintiff Forrester, for an invention in a method for reducing the leaching of lead and odor from a lead bearing waste. The '939 Patent incorporates and teaches the use of DCPDHP as a TCLP Pb and odor control agent explicitly for the Kobil incinerator bottom ash. A copy of the '939 Patent is attached hereto as Exhibit 6. Forrester owned the '939 Patent throughout the period of the Defendant WTI's infringing acts and still owns the patent.

88. On information and belief, WTI has sold and/or licensed to Kobil, in Taiwan, a method for reducing the leaching of lead from a lead bearing waste comprising incinerator ash, copper wire shredder residue and auto shredder fluff consisting of contacting said waste with monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, DCPDHP, GTSP, triple super phosphate or wet-process phosphoric acid, that embodies the inventions of the '899, '928, '178 and '939 Patents.

89. Kobil's practice of the method described in the above Paragraph would constitute infringement of the '899, '928, '178 and '939 Patents, if it occurred within the United States.

90. Kobil's extraterritorial practice of the patented method is not protected by U.S. Patent Law, or by traditional common law theories of unfair competition.

91. By its acts as above alleged, WTI misappropriated, at little or no cost, Forrester's commercially valuable methods, as claimed in the '899, '928, '178 and '939 Patents.

92. Forrester and FESI as stabilizer supplier have suffered and continue to suffer economic damage as a result of WTI's misappropriation.

JURY TRIAL DEMAND

93. Pursuant to Rule 8, Rules of the Superior Court for the State of New Hampshire, Plaintiffs hereby demand a trial by jury on all issues set forth herein that are properly triable to a jury.

PRAYER FOR RELIEF

WHEREFORE, Plaintiffs FESI and Forrester respectfully request that the Court, upon final hearing of this matter, grant the following relief against defendant WTI:

- A. Preliminarily and, after trial, permanently enjoin WTI, its agents, employees and all persons and organizations in privity, or acting in concert therewith, from (1) representing to Kobil or elsewhere that calcium phosphates, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, granular triplesuper phosphate (GTSP), dicalcium phosphate dihydrate powder (DCPDHP) and other water insoluble phosphates are covered by WTI's patents and included within WTI's WES-PHix® system; (2) selling or receiving royalties by reason of the sale of DCPDHP, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, or any water insoluble phosphate or triple superphosphate (including, but not limited to, GTSP) to Kobil; and (3) further interfering with the actual and prospective contractual relationships between FESI/Forrester and Kobil;
- B. Affirmatively require WTI, its agents, employees and all persons and organizations in privity, or acting in concert therewith, to retract any and all previous false and misleading statements to Kobil as above alleged;
- C. Affirmatively require WTI, its agents, employees and all persons and organizations in privity, or acting in concert therewith, to provide corrective advertising, at WTI's cost and expense, conspicuously stating that calcium

phosphates, monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, dicalcium phosphate dihydrate powder (DCPDHP), granular triple superphosphate and other water insoluble phosphates are not covered by WTI's patents and are not included within WTI's WES-PHix® system;

- D. Award FESI its actual damages incurred as a result of WTI's tortious interference with FESI'S contractual relations;
- E. Award FESI its actual damages incurred as a result of WTI's tortious interference with FESI'S prospective advantage;
- F. Award FESI treble and/or enhanced damages, attorneys fees and costs, as provided by New Hampshire RSA 358-A:10;
- G. Order WTI to disgorge its profits gained in violation of New Hampshire RSA 358-A:10;
- H. Permanently enjoin WTI from unlawful acts pursuant to New Hampshire RSA 358-A:10;
- I. Award FESI prejudgment and post-judgment interest; and
- J. Award to FESI any other relief, in law and in equity, to which the Court finds FESI justly entitled.

Plaintiff Forrester further respectfully requests that the Court:

- A. Preliminarily and, after trial, permanently enjoin WTI, its agents, employees and all persons and organizations in privity, or acting in concert therewith, from further misappropriating any or all of the methods embodied in the '908, '929, '899, '928, '178 and '939 Patents by offering to sell, selling, offering to license, licensing or otherwise providing any or all of the patented methods to any third

party, to be practiced outside the United States, without authorization from Forrester;

- B. Award Forrester compensatory damages in a sum to be determined at trial for WTI's misappropriation of the methods embodied in the '908, '929, '899, '928, '178 and '939 Patents;
- C. Award Forrester prejudgment and post-judgment interest; and
- D. Award to Forrester any other relief, in law and in equity, to which the Court finds Forrester justly entitled.

Dated: April 5, 2010 Respectfully submitted,

FORRESTER ENVIRONMENTAL SERVICES, INC.
and KEITH E. FORRESTER

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US005860908A

United States Patent [19]
Forrester

[11] Patent Number: **5,860,908**
[45] Date of Patent: **Jan. 19, 1999**

[54] **WATER INSOLUBLE HEAVY METAL STABILIZATION PROCESS**

5,769,938 6/1998 Ueshima et al. 588/257 X

[76] Inventor: **Keith Edward Forrester, P.O. Box 2008, Hampton, N.H. 03843-2008**

Primary Examiner—George Suchfield

[21] Appl. No.: **729,665**

ABSTRACT

[22] Filed: **Oct. 7, 1996**

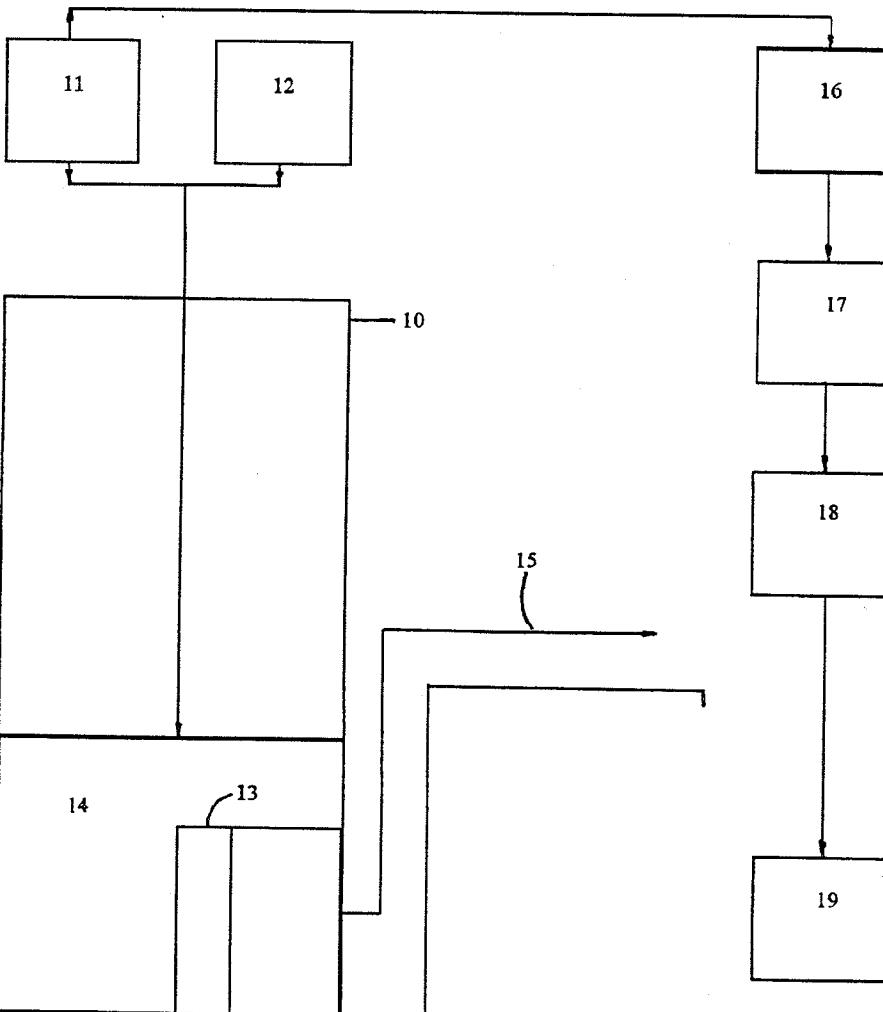
[57]

[51] Int. Cl.⁶ A62D 3/00; B09D 3/00
[52] U.S. Cl. 588/256; 405/128
[58] Field of Search 588/252, 256,
588/257; 210/768; 405/128

Ash residues produced from solid waste combustion and certain industrial residues which are sometimes contacted with water for dust control, quenched for temperature reduction or subjected to water separation methods, have lead (Pb) and other heavy metals in sufficient solubility to sometimes fail the USEPA TCLP test and other acid leaching tests. Addition of a water-insoluble precipitating agent, such as pulverized phosphate rock or a precipitating agent coated with a water-insoluble film, during waste generation or collection allows the waste to pass TCLP regulatory testing, reduces Pb leaching under acid conditions and provides a water-insoluble stabilizing seed which will remain with the residue throughout water spraying, quenching or wet processing.

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10 Claims, 1 Drawing Sheet



U.S. Patent

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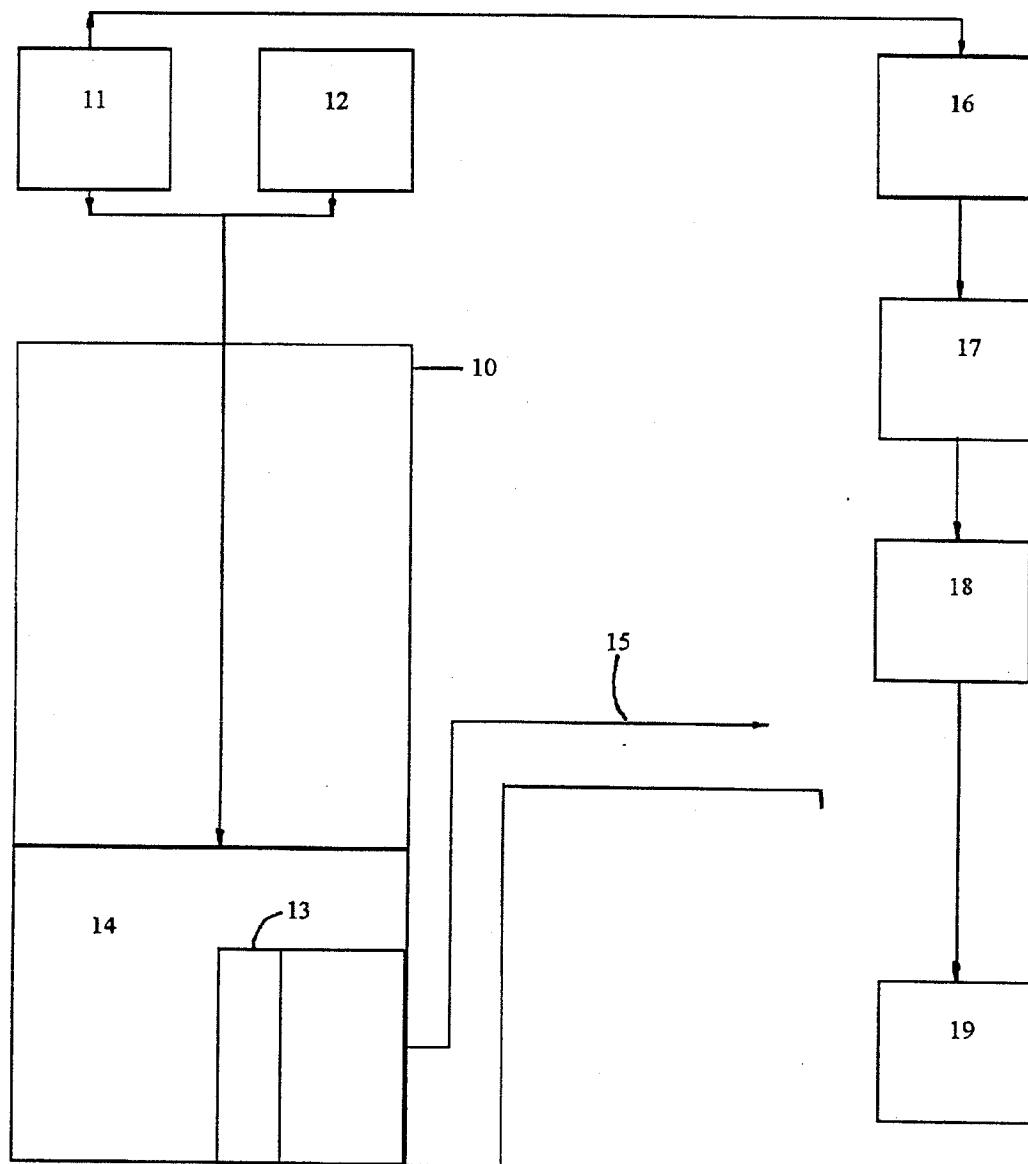


FIG. 1

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**WATER INSOLUBLE HEAVY METAL
STABILIZATION PROCESS**
FIELD OF INVENTION

This invention relates to a method for stabilizing heavy metals from solid residues, and more particularly stabilizing lead and cadmium contained in ash residues from the incineration or combustion of solid wastes, and fluff wastes produced from the shredding of wire and automobiles.

BACKGROUND OF INVENTION

The leaching of heavy metal bearing wastes and human and biological exposure to heavy metal content has long been of concern to environmental regulators and waste producers. Under the Resource Conservation and Recovery Act (RCRA) solid waste is classified by the U.S. Environmental Protection Agency (EPA) as hazardous waste if excessive amounts of heavy metals leach from the waste when tested under the Toxicity Characteristic Leaching Procedure (TCLP). EPA also regulates the land disposal of certain heavy metal bearing wastes depending on the content of the heavy metals regardless of the leaching potential. In addition, several state governments require solid wastes with elevated levels of heavy metals be disposed of as a hazardous waste. Disposal of waste at a hazardous waste landfill is typically more expensive than disposal at non-hazardous waste landfills.

To reduce the expenses associated with the landfill disposal of heavy metal leachable waste, particularly lead bearing waste, various methods to control heavy metal leaching and reduce heavy metals have been developed. These methods include the stabilization of lead bearing waste with, for example, portland cement, silicates, sulfates, water soluble phosphates and combinations thereof as well as acid digestion and subsequent extract metals recovery. However, these methods are often expensive to perform and involve complex handling equipment and operations. Additionally, some of these methods use chemicals, such as high molarity acids, which in the amounts used, are very corrosive to the waste generation and/or treatment process equipment. These methods also alter the nature of the waste which complicates the ability of the waste to be further processed. These methods also use water soluble chemicals which, upon additional wet processing of the waste, are subject to loss due to water solution stripping.

Thus a need exists for means of reducing lead leaching from the lead bearing waste which are less expensive, less damaging to equipment and allows the waste to be further processed and handled after stabilization.

SUMMARY OF INVENTION

The purpose of this invention is to increase the immobilization of heavy metals in waste contaminated materials to reduce the loss of stabilization chemicals due to waste processing and handling, and thus improve waste reuse and reducing the cost of treatment. In one embodiment, the invention provides a method of immobilizing heavy metal, e.g., lead, in a free flowing dry or wet waste which maintains its free flowing nature after immobilizing treatment. A waste is contacted with an effective amount of water insoluble immobilizing agent to reduce the leaching of the heavy metal to a level no more than regulatory limits (e.g., 5 ppm) lead as determined in an EPA TCLP test performed on the resulting treated waste as set forth in the Federal Register, vol. 55, no. 126, pp. 26985-26998, or California State

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leaching test. In another embodiment, heavy metal in a waste is immobilized such that the agent remains intact within the waste during waste wetting or handling processes. The method consists essentially of contacting the waste with a water-insoluble immobilizing agent that is capable of remaining integral to the waste matrix under normal handling conditions and remains water insoluble during wetting of the waste when quenched, sprayed or contacted with water during waste production or collection, thereby immobilizing the heavy metal. In one embodiment, heavy metal bearing residue in the form of incinerator bottom ash is, either alone or in combination with other lead bearing waste, contacted with an effective amount of a source of water for cooling and dust control of such ash and a water-insoluble precipitating agent such as pulverized phosphate rock to immobilize certain heavy metal species such that the resulting solids remaining are below TCLP regulatory limits. In a more specific embodiment, the amount of the pulverized phosphate rock is from about 0.5% to 20.0% of the ash wet weight, preferably from about 0.5% to 5.0% and more preferably from about 0.5% to 2.0%.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE shows an embodiment of the present invention in process schematic fashion showing an incinerator which allows the application of the water-insoluble phosphate rock therein prior to bottom and flyash collection.

**DETAILED DESCRIPTION OF THE
INVENTION**

The materials being treated in the present invention are heavy metal containing wastes or contaminated materials, preferably ash by solid waste combustion and/or the ferrous and non-ferrous metals normally produced along with the bottom ash, as well as shredder residues from wire chopping and auto shredding operations which produce a fine fraction of waste separated from ferrous and non-ferrous metals. Such wastes, materials and residues contain high levels of lead and cadmium which can be leached at levels in excess of 5.0 ppm (5 mg/l) and 1.0 ppm (1 mg/l) as determined by the USEPA TCLP leaching test and copper and zinc in excess of 25.0 ppm and 200.0 ppm as determined by the California state leaching test method. When dry, the initial physical character of such solid residues and ash is a free flowing particulate mass, and a virtue of the present invention is that after treatment to immobilize these metals, the solid ash residues retain their initial free flowing granular character, which is important in the handling thereof, i.e., there is no need to change handling equipment in part because the weight, density and adhesion character of the solid residue has not been significantly modified. The present invention does not modify the drainability of the ash or modify the ash sizing, which is important since the solid ash product as produced in its original form is suitable for drainage, handling, landfilling and reuse.

The following description of the present invention is couched in terms of incinerator ash only resulting from the combustion of solid waste. This corresponds to a convenient way of carrying out the present invention, but the choice of this particular description is for expository convenience only. It is to be clearly understood that variants such as treatment of a mixture of ash with other solid residues such as fluff or other solid residues, treatment of other solid wastes or solid materials such as heavy metal contaminated soils, auto shredder residue, wire chopping insulation waste, foundry sands, sandblast wastes, and ferrous and/or non-

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ferrous scrap residue after combustion, or independently treating ash and then combining it with another inert solid residue are intended to be subsumed under the present invention as claimed, as are other permutations which one skilled in the art will recognize.

Incinerators for burning trash and other solid wastes are well known to those skilled in the art. Bottom ash produced from incineration is what remains on the grate of the furnace after combustion of the waste. The bottom ash is often a granular character and somewhat glassy in nature, and also includes ferrous and non-ferrous metals which are often recovered from the bottom ash by mechanical and electro-mechanical means such as screening, electromagnetic and eddy current separation. The other inert material resulting from combustion of solid wastes is flyash, a finer material which becomes airborne in the furnace and is captured in various forms of air pollution control units such as fabric filters, electrostatic precipitators, cyclones and combinations thereof. The bottom ash produced during the combustion of waste is sometimes mixed with the flyash in order to allow for use of a mixed combined ash disposal system. The bottom ash discharges from the bottom of the incinerator furnace grate at high temperatures ranging from 1500 to 2500 degree Fahrenheit, and thus requires cooling by air and/or water prior to further handling. The most common method of ash cooling is by water quenching in a drag tank or ram discharging tank which also acts as a seal to restrict air flow into the base of the furnace. The bottom ash is expelled from the wet quenching tank by means of either a pushing ram or drag flights, both which allow a controlled period of time for ash to be wetted and cooled in the bath of water prior to discharging to a removal conveyor. Both of these common ash quench expelling methods incorporate inclined drainage after the bath which allows quenching waters not retained, adsorbed or otherwise captured by the bottom ash to be returned to the quench tank. The water retained by the bottom ash and water also lost to evaporation due to the water seal exposure to heat is made up by new process water called make-up water. Referring to the FIGURE, the bottom ash primary contact tank 10 is one possible contact point for applying the water-insoluble precipitating agent to the bottom ash, with the water-insoluble precipitating agent 11 being added to the tank 10 through a water make up supply 12 at a rate to maintain a desired concentration of suspended water-insoluble precipitating agent in solution. The bottom ash 13 would be removed by dischargers 14 at a rate set for control of ash mass release from the incinerator unit as well as allowing a desired retention time of ash in contact with the water-insoluble precipitating agent solution. The water-insoluble precipitating agent solution concentration and retention time selection could vary depending on the desired reduction of heavy metal content in the ash as well as the need for reduction of soluble metals as evaluated under TCLP and other state regulatory test methods. The immobilization of heavy metals from the ash can also be completed in a tank reactor separate from the quench tank, thus being conducted in a batch mode as compared to the continuous flow mode of the ash quenching tank. After contact with the water-insoluble precipitating agent solution tank for a controlled period of time, the bottom ash is subjected to a dewatering step, preferably by gravity drainage on an inclined drag chain bed 15 or an inclined ram or by overhead drainage if the ash is placed into a batch reactor separate from the furnace ash wet quench tank. The water-insoluble precipitating agent 11 could also be injected via pneumatic blowing means to the intake side ducting 16 of the facility air pollution collection

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device 17, and thereafter conveyed 18 by mechanical means to a discharge point 19 with or without combination with the stabilized bottom ash.

Any convenient source of water-insoluble precipitating agent or water-soluble agent coated with a water-insoluble covering can be used in the practice of this invention. The immobilizing agent when contacted with a heavy metal containing waste or contaminated material should remain integral to the waste matrix during normal handling thereof and during wetting of the waste or contaminated material when quenched, sprayed or contacted with water during waste production or collection. The insoluble precipitating agent can be applied to the bottom ash in either a slurry or dry form. The water-insoluble precipitating agent could include solid phosphates (e.g., phosphate rock, superphosphates, Triple Superphosphate), carbonates (e.g., calcium carbonates), carbon, sulfides, magnesium oxide and combinations thereof which resist water solubility either by natural character such as pulverized phosphate rock or by engineered surface coating application onto otherwise water-soluble agent surfaces. In one embodiment, Triple Superphosphates, Superphosphates, dolomitic lime, lime, silicate powders, carbonates, sulfates and sulfides can be surface coated to minimize the premature release of stabilizing chemicals, as described below. A coating of polymer over otherwise water-soluble Triple Superphosphate (TSP) is one example of a coated chemical used currently for time release control of phosphate and nitrogen into potted and non-potted soils for rose and flower growers. In all applications, the selection of water-insoluble precipitating agent or water insoluble coatings over water-soluble agents is key in order to minimize the premature release of stabilizing chemicals during the application or exposure of the ash and/or material to rainwater, rinsing water, separation water, processing water, and/or quenching water, and to allow the release of stabilization chemicals to occur only during the exposure of the blended waste and/or material to organic acids such as dilute acetic acid or buffered acetic and/or citric acids which simulate landfill leaching conditions. Accordingly, the release of water insoluble chemicals (precipitating agent) will occur during the stabilized waste and/or material exposure to TCLP or California WET extraction fluids, as both fluids are designed to simulate the leachability of a subject waste under decomposing landfill leaching conditions. The preferred water-insoluble stabilization chemical for Pb bearing wastes and/or materials is pulverized phosphate rock such as North Carolina NATURAL PHOSPHATE and similar pre-acidulated phosphate mineral.

The amount of water-insoluble precipitating agent to be added to the ash or other solid residues combined with ash to ensure adequate TCLP immobilization will depend on such variables as bottom ash alkalinity, heavy metal content, surface character and desired reduction of TCLP leaching levels for heavy metals. It is believed that a water-insoluble phosphate rock of 0.5% by wet weight of ash to 1.0% by weight added in the ash production line prior to collection and dewatering will be sufficient to convert enough of the heavy metals such that TCLP levels are below regulatory limits of 5.0 ppm for Pb and 1.0 ppm for Cd. However, the foregoing is not intended to preclude yet higher or lower usage of water-insoluble precipitating agent or location of application as found reasonable or necessary given regulatory criteria or differences due to ash initial metals content or character.

It has been found that the TCLP character of ash varies widely from facility location and ash production type, thus

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causing uncertainty amongst regulators and potential ash users as to the leaching and total metals character of the ash. The present invention provides a means to reduce the TCLP variability of ash, thus improving the reusability and disposal options for ash.

The examples below are merely illustrative of this invention and are not intended to limit it thereby in any way.

EXAMPLE 1

In this example, bottom ash from a solid waste combustion facility using an ash quench tank was first subjected to a baseline TCLP analyses in order to define the character of the ash prior to stabilization and processing. The bottom ash baseline sample was subject to the Toxicity Characteristic Leaching Procedure (TCLP) as set forth in the Federal Register Vol. 55, No. 61 (Mar. 29, 1990) which corresponds in pertinent part to the procedure set forth in Federal Register, Vol. 55, No. 126, pp 26985-26998 (Jun. 29, 1990), both of which are hereby incorporated by reference. This test procedure is also referenced in EPA SW 846, 3rd Edition. The TCLP test produces an aliquot filtered solution containing soluble metals which were analyzed by ICP-MS. The bottom ash was then subjected to a 0.5%, 1.0% and 2.0% by weight basis addition of pulverized phosphate rock (Rock-P) and 0.5%, 1.0% and 2.0% polymer coated triple superphosphate (Poly TSP), and thereafter subjected to the TCLP test. The ash baseline and post-stabilized Pb concentrations are presented in Table 1 in rounded average values. The results clearly confirm the suitability of water-insoluble phosphates and polymer coated phosphates for incinerator bottom ash TCLP Pb stabilization.

TABLE 1

RECIPE	Pb TCLP RESULTS (ppm)
Baseline	13.5
0.5% Rock-P	5.6
1.0% Rock-P	1.1
2.0% Rock-P	0.2
0.5% Poly TSP	8.3
1.0% Poly TSP	4.2
2.0% Poly TSP	0.5

EXAMPLE 2

In this example, wire chopping waste insulation produced from a facility which separates wire insulation from copper and aluminum wire for resale of the copper and aluminum was first subjected to a baseline TCLP analyses in order to define the character of the waste insulation prior to stabilization and processing. The waste insulation was then subjected to a 0.5%, 1.0% and 2.0% by weight basis addition of pulverized phosphate rock (Rock-P) and 0.5%, 1.0% and 2.0% polymer coated triple superphosphate (Poly TSP), and thereafter subjected to the TCLP test. Given that the waste insulation is often subjected to wet quenching in order to recover additional amounts of copper and aluminum by floating PVC and PE from the heavier metal fraction, the insulation after stabilization was also subjected to water quenching and TCLP tests to confirm that the phosphate seed remained with the insulation and did not significantly solubilize or react with the water bath thus reducing TCLP leaching control. The waste baseline and post-stabilized Pb concentrations are presented in Table 2 in rounded average values. The results clearly confirm the suitability of water-insoluble phosphates and polymer coated phosphates for TCLP Pb insulation stabilization in either a dry or wetted

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application. The slight numerical variability noticed from the dry to wet waste TCLP testing is most likely due to the heterogeneous nature of Pb content within the insulation from a gram-to-gram basis, and is not expected to be a function of wash-out of fine phosphates from the wet separation process or changes in surface reactivity of the water insoluble phosphates.

TABLE 2

RECIPE	Pb RESULTS DRY (ppm)	Pb RESULTS WET (ppm)
Baseline	31.0	NA
0.5% Rock-P	15.6	14.3
1.0% Rock-P	5.1	5.3
2.0% Rock-P	2.5	2.7
0.5% Poly TSP	25.4	27.5
1.0% Poly TSP	12.8	14.7
2.0% Poly TSP	3.7	4.1

EXAMPLE 3

In this example, wire chopping waste insulation was subjected to a 0.5%, 1.0% and 2.0% by weight basis addition of non-pulverized phosphate rock and thereafter subjected to the TCLP test. This non-pulverized phosphate rock was investigated in order to determine impact of pulverization of rock on the availability of surface active phosphate sites for stabilization of Pb under the TCLP test as well as the impact of pulverization on the control of sifting of chemical from the waste insulation. The non-pulverized phosphate rock used had a Tyler size distribution on 100% passing at 14 mesh, 97% pass at 35 mesh, 49% pass at 65 mesh, 19% pass at 100 mesh and 1% pass at 200 mesh, as compared to the pulverized rock used in Examples 1 and 2 which had 85% passing at 200 mesh. The application of the non-pulverized phosphate rock to the dry wire insulation was found to sift out 50% to 60% of the addition with a single tumble in a 1000 ml container of 100 grams of wire insulation and a 2% application of rock. This sifting phenomena was considered troublesome, as the stabilization chemical was not staying integrated within the waste regardless of mixing methods used. A laboratory simulation of roadway hauling of the mixed dry insulation and the rock, pulverized rock and lower density triple superphosphate (TSP) prills were conducted in order to determine if the phosphate rock, pulverized rock and/or TSP would sift away from the upper layers of the waste insulation and thus cause the upper layer of a truck load of stabilized waste to fail a composite TCLP sample analyses as received at a landfill after vibrations from hauling. The simulation involved applying a well mixed phosphate rock, pulverized rock and TSP at 2% wet weight basis to dry insulation waste on a shaker table set at 120 strokes per minute. A surface composite waste sample was then collected from the table samples for TCLP analyses. The waste baseline and post-stabilized Pb concentrations are presented in Table 3 in rounded average values. The results clearly confirm that water-insoluble non-pulverized phosphates were not as effective as pulverized phosphate rock or TSP in passing TCLP and that the non-pulverized rock allowed for sifting which greatly increased TCLP levels of samples collected from a source subjected to vibration after application of the phosphate rock. The pulverized rock coated the insulation and remained as a uniform coating on the waste regardless of vibration. The TSP prills also remained integrated within the waste insulation and did not sift, yet the prills did not adhere to the insulation as did the pulverized phosphates. The prills remained uniform within the waste insulation due to their density of 55 to 60 lbs per

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cubic foot which was very similar to the waste insulation of 45 to 50pcf and their semi-round shape and size of 6 to 16 Tyler mesh which allowed for the prills to hold between bridges of waste insulation without separating. The prills also have an angle of repose of 25 to 30 degrees and a somewhat irregular surface which improves bridging behavior of the prill within the insulation waste matrix.

TABLE 3

RECIPE	Pb DRY (ppm)	Pb Sifted (ppm)
Baseline	31.0	NA
0.5% Rock	30.5	32.0
1.0% Rock	20.1	29.0
2.0% Rock	14.5	27.4
0.5% Rock-P	15.6	16.3
1.0% Rock-P	5.1	5.4
2.0% Rock-P	2.5	2.2
0.5% Poly TSP	25.4	25.5
1.0% Poly TSP	12.8	11.8
2.0% Poly TSP	3.7	4.1

EXAMPLE 4

In this example, flyash scrubber residue from a refuse-derived fuel solid waste combustion facility using an ash DUSTMASTER mixing and conditioner for ash wetting was first subjected to a baseline TCLP analyses in order to define the character of the ash prior to stabilization and processing. The flyash was subjected to a 2.0% by weight basis addition of pulverized phosphate rock (Rock-P) by injection of the Rock-P into the facility gas collection device prior to the collection of flyash onto a facility baghouse filtering device. The flyash and Rock-P were effectively mixed together in the gas stream ahead of the baghouse filters which collect the flyash residue after combustion of municipal solid waste, and the flyash and Rock-P combination was then collected in facility ash collection hoppers and transferred to the facility DUSTMASTER mixer for water addition as dust control. After mixing in the DUSTMASTER the flyash and Rock-P were thereafter subjected to the TCLP test. The flyash baseline and post-stabilized Pb concentrations are presented in Table 1 in rounded average values. The results clearly confirm the suitability of water-insoluble phosphates for incinerator flyash scrubber residue TCLP Pb and Cd stabilization.

TABLE 4

RECIPE	Pb TCLP RESULTS (ppm)
Baseline	28.5
2.0% Rock-P	2.1

The foregoing results readily establish the operability of the present process to reduce leachable soluble metals in waste residues and materials and to provide a chemical stabilizing agent which remains effective and non-reactive under water quenching conditions and under waste sifting conditions. The degree of reduction of heavy metal leaching can be regulated by the operator and would likely depend on the baseline character of the waste as well as regulatory criteria relative to the waste reuse or disposal options. The above described process allows for a wide range of operations options and is highly flexible given ones ability to adjust process variables such as water insoluble precipitation

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election and dosages, wetting degree and application point of stabilization chemical. It is expected that the most common element of regulatory concern, Pb, will be reduced and controlled to suitable TCLP levels using a 0.5 to 2.5 weight basis addition of water-insoluble agent.

10 It will be apparent from the foregoing that many other variations and modifications can be made in the methods and the compositions herein before described, by those having experience in this technology, without departing from the concept of the present invention. Accordingly, it should be clearly understood that the methods and compositions referred to herein in the foregoing description are illustrative only and are not intended to have any limitations on the scope of the invention.

15 I claim:

1. A method of immobilizing heavy metal in a free flowing dry or wet waste which maintains its free flowing nature after immobilizing treatment, said method consisting essentially of:

25 contacting a waste with an effective amount of water insoluble immobilizing agent to reduce the leaching of the heavy metal to a level no more than regulatory limits as determined in an EPA TCLP test performed on the resulting treated waste as set forth in the Federal Register, vol 55, no. 126, pp. 26985-26998.

30 2. The method of claim 1, wherein the water-insoluble agent is selected from the group consisting of natural minerals, phosphate rock, pulverized phosphate rock, calcium carbonates, magnesium oxides and carbon.

35 3. The method of claim 1, wherein the water-insoluble agent comprises a water-soluble agent having a water-insoluble coating thereon, wherein the water-soluble agent is selected from the group consisting of triple superphosphates, superphosphates, dolomitic lime, lime, silicate powders, carbonates, sulfates and sulfides, wherein an applied surface coating onto the water-soluble precipitating agent provides a surface character which is water-insoluble.

40 4. The method of claim 1, wherein the waste is selected from the group consisting of bottom ash, flyash, scrubber residue and combinations thereof resulting from the combustion of solid waste.

45 5. The method of claim 1, wherein the waste is selected from the group consisting of shredder fluff resulting from the shredding of automobiles, shredding of wire, shredding of white goods and combinations thereof.

6. The method of claim 1 wherein the heavy metal is selected from the group consisting of lead, cadmium, copper and zinc.

55 7. A method of immobilizing heavy metal in a free flowing dry or wet waste or heavy metal contaminated material which maintains its free flowing nature after immobilizing treatment, said method consisting essentially of:

contacting the waste or contaminated material with an effective amount of an immobilizing agent to reduce the leaching of the heavy metal to a level no more than regulatory limits as determined in a California State leaching test or an EPA TCLP test performed on the resulting treated waste or contaminated material, as set forth in the Federal Register, vol. 55, no. 126, pp. 26985-26998; wherein the immobilizing agent is selected from the group consisting of phosphate rock, pulverized phosphate rock, triple superphosphate, superphosphate, silicate, magnesium oxide, sulfates, sulfides and lime, said immobilizing agent being

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capable of remaining integral to the waste or contaminated material matrix during wetting of the waste or contaminated material when quenched, sprayed or contacted with water during waste production or collection, thereby immobilizing the heavy metal.

8. The method of claim 7, wherein the waste is selected from the group consisting of bottom ash, flyash, scrubber residue and combinations thereof resulting from the combustion of solid waste.

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9. The method of claim 7, wherein the waste is selected from the group consisting of shredder fluff resulting from the shredding of automobiles, shredding of wire, shredding of white goods and combinations thereof.

10. The method of claim 7, wherein the waste is contacted with at least one immobilizing agent in the amount of 0.01% to 20.0% by weight of agent based on the total waste.

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US006050929A

United States Patent [19]**Forrester**

[11] **Patent Number:** **6,050,929**
 [45] **Date of Patent:** **Apr. 18, 2000**

[54] **METHOD FOR STABILIZING HEAVY METAL BEARING WASTE IN A WASTE GENERATION STREAM**

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[21] Appl. No.: **08/729,832**

[22] Filed: **Oct. 8, 1996**

Related U.S. Application Data

[63] Continuation of application No. 08/132,926, Oct. 7, 1993, abandoned.

[51] **Int. Cl.⁷** **A62D 3/00; B09B 1/00**

[52] **U.S. Cl.** **588/256; 405/128; 588/249**

[58] **Field of Search** **405/128, 129; 588/249, 256, 257**

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[57]

ABSTRACT

Heavy metal bearing products during production, processing and/or handling, and/or in landfills, storage or retention areas are stabilized prior to the generation or management as a waste by applying heavy metal stabilizing agents into the product stream thus avoiding complex and costly processing and treatment of waste under hazardous waste regulations.

20 Claims, No Drawings

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1**METHOD FOR STABILIZING HEAVY METAL BEARING WASTE IN A WASTE GENERATION STREAM****RELATED APPLICATION**

This application is a continuation of application Ser. No. 08/132,926 filed on Oct. 7, 1993, now abandoned, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The invention relates to the pre-waste production stabilization of heavy metal bearing hazardous and/or solid waste subject to direct aqueous analyses, solid phase acid leaching, distilled water extraction, the California Citric Acid Leaching test and other citric leaching tests and/or Toxicity Characteristics Leaching Procedure, by use of water soluble stabilizing agents such as flocculants, coagulants and heavy metal precipitants including sulfides, carbonates and phosphates. The stabilizing agents, are added to the material production, development or process prior to the first generation of any waste material. This approach responds directly to the RCRA requirement that exempt treatment of hazardous wastes be in a totally-enclosed fashion, as well as allowing for stabilization of heavy metal bearing particles to occur in a pre-mixed and as-produced manner in order to assure consistent and accurate ability to pass the waste extraction method of interest.

The combination of pre-waste materials with treatment additives such as epoxy agents, precipitants, flocculating agents, and granular activated carbon particles provides for as-produced stabilization where the need for post-produced waste mixing, feed controls, collection as a waste, storage manifesting, and expensive and burdensome post waste treatment is obviated.

One specific use under evaluation and study by the inventor involves the seeding of black beauty and other sand blast grit materials with various forms of air entrainable particle precipitants and minerals which would provide for a integral mixed soluble phase of heavy metal precipitant within the post-sandblast waste generated that would be released under a leaching exposure of the waste after sandblasting of Pb, Cu, Zn, and other metals bearing in paints, such as for ship yards. The advantage of the pre-waste stabilizer additive here is that the collection of the heavy metal bearing waste will not be as necessary for environmental and/or TCLP waste handling reasons, and upon any such collection the grit and paint products will have been seeded thus requiring no RCRA permitting for hazardous waste treatment or handling.

Another specific use of pre-waste stabilization involves the injection of particulate water soluble precipitants, flocculants, coagulants and/or mineral salts directly into the processing lines of auto-shredders and wire-chopping systems such that the first generation point of fines, dust, wastes, fluff and/or plastics have been seeded with such stabilizing agents and thus the produced waste will pass TCLP criteria and thus be exempt from RCRA Part B permitting.

The general approach of the pre-waste stabilization technology described herein can be utilized in many waste generation systems such as incinerators producing ash materials, wastewater sludge production, drilling tailings production and storage tank sludge collection. The specific application of stabilization agents into the process prior to the generation of wastes would be designed and operated on a case-by-case basis.

2**DESCRIPTION OF RELATED TECHNOLOGY**

Leaching of heavy metal bearing wastes and direct discharges of heavy metal bearing wastewaters has been of concern to environmental regulators and waste producers since the 1970's and the promulgation of the Resource Conservation and Recovery Act (RCRA) in 1979 and with various health officials. Under RCRA, solid wastes may be considered hazardous if the waste leaches excessive heavy metals under the Toxicity Characteristic Leaching Procedure (TCLP). In addition, there exist various states such as California, Minnesota and Vermont which require additional leaching tests on solid waste in order to classify the waste and direct the more heavy metal leaching wastes to hazardous waste landfills.

In order to avoid having solid waste s be required to be handled at more expensive hazardous waste landfills, various researchers and solid waste businesses have investigated and methods to control the leaching of heavy metals such as lead from the solid waste. The art has looked at the control of leaching by ex-situ methods involving portland cement, silicates, sulfates, phosphates and combinations thereof. See U.S. Pat. Nos. 4,629,509 (calcium sulfide); 4,726,710 (sodium sulfur oxide salt); which are incorporated by reference.

SUMMARY OF THE INVENTION

Existing heavy metal treatment processes are designed and operated in a post-waste production mode or remediation mode and thus ignore the advantages of stabilizing agents into the product stream prior to or during waste production.

It is an object of the invention to provide a method that effectively treats any heavy metal bearing wastes by the use of water soluble stabilizing agents such as dry alum, activated carbon and/or heavy metal precipitants (e.g. sulfides and phosphates) such that the stabilized waste will resist the leaching of copper, zinc, lead, cadmium and other heavy metals.

It is another object of the invention to provide a method of in-line stabilization which allows for hazardous and solid waste treatment without the need for the use of any post-waste production mixing device and for the treated waste to remain free flowing.

It is a further object of the invention to provide for the mix of treatment chemicals to be added directly to the material generated prior to a waste classification and thus avoid the need to treat the waste as a hazardous waste under RCRA and avoid the need for treatment permitting.

In accordance with these and other objects of the invention, which will become apparent from the description below, the process according to the invention comprises:

adding a stabilizing agent, for example, a flocculant, coagulant and/or precipitant, or mixture thereof, such as ferric chloride, alum, ferric sulfate, feldspar, clays, activated alumina, phosphates or wastes comprising these elements, in sufficient quantity such that the treatment chemicals are dispersed onto or into the pre-waste material such that the produced waste will pass the regulatory limits imposed under the acid leaching tests, similar aggressive or natural and distilled water leaching environments.

Providing for a sufficient pre-waste seeding of stabilizing agents assures passage of TCLP leaching criteria and/or other relevant leaching tests in order to characterize the waste as non-hazardous and/or to reduce the solubility

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of the heavy metal bearing waste to a point considered suitable by the appropriate local, state and/or federal leaching criteria.

DETAILED DESCRIPTION

One of the most costly environmental tasks facing industry in the 1990's will be the clean-up and treatment of heavy metal bearing wastes, both solid and hazardous, at old dump sites, storage areas and retention areas and at existing waste generation sites such as process facilities or incinerators throughout the world. Depending on the specific state and federal regulations, those wastes will be classified as either solid, special or hazardous. The management options for the waste producer vary greatly depending on the waste classification and the regulatory requirements associated with that classification. The most stringent waste classification is that of hazardous.

There exist various methods of stabilizing and solidifying heavy metal bearing hazardous wastes. The most common method, using portland cement for physical solidification, is common knowledge in the environmental engineering field. There exist several patented processes for hazardous waste treatment such as using carbonates, polysilicates, phosphates and versions of portland cement. These patented methods and the use of portland cement all recognize the need to control chemistry and provide for mixing of the waste and the treatment chemicals in order to control heavy metal solubility as tested by the TCLP Federal acetic acid leaching test by either precipitation of the heavy metal into a less soluble compound or the physical encapsulation of the waste and surface area reduction.

Wastes subject to regulation are usually tested via the USEPA TCLP extraction method. The TCLP extraction method is referred to by the USEPA SW-846 Manual on how to sample, prepare and analyze wastes for hazardousness determination as directed by the Resource Conservation and Recovery Act (RCRA). The TCLP test by definition assumes that the waste of concern is exposed to leachate from an uncovered trash landfill cell, thus the TCLP procedure calls for the extraction of the waste with a dilute acetic acid solution which simulates co-disposal with decaying solid waste.

In the method of invention, a stabilizing agent can be used to reduce the leachability of heavy metals, such as lead, copper, zinc, chromium and cadmium, from a heavy metal bearing waste by contacting the stabilizing agent with the product from which the waste is generated, or with the generated waste while in the waste generation stream.

Wastes stabilizable by this method include various types of waste materials from which heavy metals can leach when subject to natural leaching, runoff, distilled water extraction, sequential extraction, acetic acid, TCLP and/or citric acid leaching or extraction. Examples of such heavy metal leachable wastes, include, for instance, wire chop waste, auto shredder fluff, sludges from electroplating processes, sand blast waste, foundry sand, and ash residues, such as from electroplating processes, arc dust collectors, cupola metal furnaces and the combustion of medical waste, municipal solid waste, commercial waste, sewage sludge, sewage sludge drying bed waste and/or industrial waste.

In one embodiment, a stabilizing agent is contacted with the product prior to generating a waste from the product. For example, the stabilizing agent can be contacted with the product while the product is in a product storage pile and/or while the product is in a waste generation stream. Further, the stabilizing agent can be directed onto the product while

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in said stream and/or onto the waste generation equipment which transports the product and/or operates upon the product to form the heavy metal bearing waste. For example, to reduce heavy metal leachability from auto shredder wastes, such as fluff, a stabilizing agent is added prior to generation of the wastes, which are collected after baghouse and cyclone collectors, including adding the stabilizing agent to auto shredder units, to conveying units or to handling units.

In another embodiment, heavy metal leachability from wastes, which are generated by chopping insulated wires, such as wire or fluff mixed with PVC, or paper, which surrounded the wire, are reduced by adding a stabilizing agent to the waste generation stream. The stabilizing agent can be added to the wire prior to, or after, primary and/or secondary choppers, separating beds, pneumatic lines, cyclones or other handling or processing equipment.

In yet another embodiment, the leachability of waste, generated from sand blasting a surface painted with heavy metal bearing paint, is reduced by contacting a stabilizing agent with the paint particles as the paint particles are generated by the sand blasting. The stabilizing agent can be blended with the grit used for sand blasting prior to blasting the painted surface, or coated onto the painted surface prior to blasting with the grit.

The existing hazardous waste treatment processes for heavy metal bearing wastes fail to consider the use of pre-waste stabilizer seeding and fail to design a treatment with the expectation of using the TCLP extractor as a miniature Continuous Flow Stirred Tank Reactor (CFSTR) in which complex solubility, adsorption, substitution, exchange and precipitation can occur as well as macro-particle formations. The invention presented herein utilizes the TCLP, WET and/or distilled leaching (DL) extractor as a continuous stirred tank reactor similar to that used in the wastewater industry for formation of flocculants, coagulants and precipitant reactions. In addition, the invention presented herein utilizes the post-extraction filtration with 0.45 micron filters as the method of formed particle capture and removal similar to that conducted by rapid sand filtrators used within the wastewater and water treatment fields.

Existing heavy metal treatment processes are designed and operated relying upon a post-waste production treatment. This approach ignores the regulatory, process, handling and permitting advantages of combining stabilizing agents such as retaining matrixes, coagulants and precipitants with the material to be wasted prior to such waste activity.

The ratio and respective amount of the applied stabilizing agent, added to a given heavy metal bearing material will vary depending on the character of such heavy metal bearing material, the process in which the waste is produced, heavy metal content and treatment objectives. It is reasonable to assume that the optimization of highly thermodynamically stable minerals which control metals such as Pb will also vary from waste type, especially if the waste has intrinsic characteristics available forms of Cl, Al(III), sulfate and Fe.

The current methods incur an extensive cost in assuring waste-to-treatment additive mixing with heavy equipment, waste handling and excavation. The invention presented herein changes that basis, and stands on the principle that the waste pre-seeding will suffice for any and all form of mixing and that regulators will allow for such seeding such that produced rainfall or simulated rainfall would carry the treatment chemical to the areas which, by natural leaching pathways, demand the most epoxy, flocculant, coagulant and precipitant treatment. Thus, for stabilization of heavy metal

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within, a stabilizing agent is added to the top of the waste pile and is then dispersed into said pile by leaching. Alternately, a stabilizing agent can be tilled into the first several feet depth of the product in a product pile, thereby allowing a time release of the stabilizing agent into the product pile and leaching pathways. The leaching can be natural, such as leaching resulting from rainfall, and/or the leaching can be induced, such as by spraying or injecting water at the surface of the product pile or below the surface of the product pile. The present invention also utilizes the mixing time and environment provided within the extraction device, thus deleting the need for the treatment additives to be mixed within the field. The sampling population required under SW-846 in addition to the mixing within the extractor provide for ample inter-particle action and avoid the need for expensive bulk mixing used with cements and common precipitant treatments now used on full scale waste treatment and site remediation activities.

EXAMPLE 1

In this first example, a medium grit sand blast was mixed with agglomerated Diammonium Phosphate prior to sand blasting a Pb bearing paint. As shown in Table 1, the grit was initially subject to TCLP leaching without the pre-waste treatment and secondly with 4 percent by weight Diammonium Phosphate. The results show that the combination of grit blast black beauty material and dry agglomerated phosphate met the regulatory limits of 5.0 ppm soluble Pb under the TCLP acid leaching test. The extraction used a 1000 ml tumbler and extraction fluid of TCLP1 in accordance with the TCLP procedure. Pb was analyzed by ICP after filtration of a 100 ml aliquot through a 45 micron glass bead filter.

TABLE 1

<u>Pb from Sand Blast Residues Subject to TCLP Leaching</u>	
Untreated	4% DIAMMONIUM PHOSPHATE
47 ppm	<0.05 ppm

EXAMPLE 2

In this example, a copper wire waste was mixed on-line with Triple Super Phosphate prior to separation of the wire from the housing through a chopping line and thus prior to any generation of waste. The addition of Triple Super Phosphate was controlled by a vibratory feeder with a slide gate to control the volumetric rate of Triple Super Phosphate to the sections of wire passing by on a vibratory conveyor. After the on-line mixture, the wire and additive were subject to high speed chopping and air separation of the plastic housings and paper off of the copper wire. At this point in the process, the wire is considered a product and thus exempt from TCLP testing. The removed plastic and paper is lead bearing, and unless treated as above, is considered a hazardous waste. The combination of the wire waste and the Triple Super Phosphate resulted in a waste which passed TCLP testing, and thus allowed to be managed as a solid waste or for reuse and recycling.

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TABLE 2

<u>Wire Chopping Wastes Subject to TCLP Leaching</u>		
Untreated	4% Triple Super Phosphate	
8 ppm Pb	<0.5 ppm Pb	

From the above examples, it is apparent that a large number of combinations of products and treatment additives could be mixed prior to the generation of the product waste in order that the waste as generated would contain the sufficient quantity and quality of heavy metal stabilizing additives such that the waste as tested by TCLP would pass regulatory limits and thus avoid the need for post-waste production stabilization. The exact combination of stabilizing additives for each waste would be determined from evaluating local waste products and/or chemical supplies and conducting a treatability study using such mixtures that produces the end objective of soluble heavy metal control within the produced waste material at the most cost efficient manner. The exact mix recipe and dosage would probably vary due to the waste stream as shown in the above examples, and will vary depending on the aggressiveness of the leaching test or objective for waste stabilization.

What is claimed is:

1. A method for stabilizing a heavy metal in a heavy metal containing material to reduce leaching of the heavy metal therefrom when said material is exposed to natural or induced leaching conditions, comprising:

contacting heavy metal containing material with a stabilizing agent that binds to the heavy metal to form a heavy metal complex when exposed to natural or induced leaching conditions; and

processing the heavy metal containing material and stabilizing agent through waste stream equipment to produce processed waste in which the heavy metal is complexed to the stabilizing agent when exposed to natural or induced leaching conditions, wherein leaching of the heavy metal from the processed waste is reduced.

2. The method of claim 1, wherein the heavy metal is selected from the group consisting of copper, zinc, lead, cadmium and chromium.

3. The method of claim 1, further comprising selecting the stabilizing agent from the group consisting of flocculants, coagulants, precipitants, complexing agents, epoxy agents and adsorbents.

4. The method of claim 1, further comprising selecting the stabilizing agent from the group consisting of phosphates, carbonates, silicates and sulfides.

5. The method of claim 4, wherein the phosphate is triple super phosphate, diammonium phosphate, phosphate rock or crop production phosphate.

6. The method of claim 1, wherein the waste generation equipment is an auto-shredder or wire-chopping system.

7. The method of claim 1, further comprising performing the contacting step before and/or as the heavy metal containing material is processed through the waste stream equipment.

8. The method of claim 1, further comprising testing the leachability of the heavy metal from the processed waste by performing a test selected from the group consisting of Toxicity Characteristic Leaching Procedure, California citric acid leaching test and citric acid leaching test.

9. A method for stabilizing heavy metal contained in insulation wire waste to reduce leaching of the heavy metal

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therefrom when said insulation wire waste is exposed to natural or induced leaching conditions, comprising:

contacting insulation wire containing heavy metal with a stabilizing agent that binds to the heavy metal to form a heavy metal complex when exposed to natural or induced leaching conditions; and

processing the insulation wire and stabilizing agent through a wire chopping system to produce chopped insulation wire waste in which the heavy metal is complexed to the stabilizing agent when exposed to natural or induced leaching conditions, wherein leaching of the heavy metal from the chopped insulation wire waste is reduced.

10. The method of claim 9, further comprising selecting the stabilizing agent from the group consisting of phosphates, carbonates, silicates and sulfides.

11. The method of claim 10, wherein the phosphate is triple super phosphate, diammonium phosphate, phosphate rock or crop production phosphate.

12. The method of claim 10, wherein the stabilizing agent is triple super phosphate.

13. The method of claim 9, further comprising performing the contacting step before and/or as the heavy metal containing material is processed through the wire chopping system.

14. The method of claim 9, further comprising testing the leachability of the heavy metal from the chopped insulation wire waste by performing a test selected from the group consisting of Toxicity Characteristic Leaching Procedure, California citric acid leaching test and citric acid leaching test.

15. A method for stabilizing a heavy metal in autoshredder waste to reduce leaching of the heavy metal therefrom when

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said waste is exposed to natural or induced leaching conditions, comprising:

contacting heavy metal containing material with a stabilizing agent that binds to the heavy metal into form a heavy metal complex when exposed to natural or induced leaching conditions; and;

processing the heavy metal containing material and stabilizing agent through autoshredding equipment to produce autoshredder waste containing heavy metal in which the heavy metal is stabilized therein when exposed to natural or induced leaching conditions, wherein leaching of the heavy metal is reduced.

16. The method of claim 15, further comprising selecting the stabilizing agent from the group consisting of phosphates, carbonates, silicates and sulfides.

17. The method of claim 16, wherein the phosphate is triple super phosphate, diammonium phosphate, phosphate rock or crop production phosphate.

18. The method of claim 15, wherein the stabilizing agent is triple super phosphate.

19. The method of claim 15, further comprising performing the contacting step before and/or as the heavy metal containing material is processed through the autoshredding equipment.

20. The method of claim 15, further comprising testing the leachability of the heavy metal from the autoshredder waste by performing a test selected from the group consisting of Toxicity Characteristic Leaching Procedure, California citric acid leaching test and citric acid leaching test.

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United States Patent [19]**Forrester**

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[54] **STABILIZATION OF LEAD BEARING WASTE**

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[21] Appl. No.: **318,538**

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[52] U.S. Cl. 588/256; 210/751; 588/260;
588/901

[58] Field of Search 405/128, 129;
588/236, 256, 260, 901; 210/751

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[57] **ABSTRACT**

A method is disclosed for reducing the leaching of lead from a lead bearing waste. The method includes contacting the waste with a water soluble phosphate and a complexing agent, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in the waste, thereby reducing the leaching of lead from the waste as determined by a leach test performed on the waste.

22 Claims, No Drawings

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STABILIZATION OF LEAD BEARING WASTE

RELATED APPLICATIONS

This is a continuation-in-part of U.S. Ser. No. 8/038,812 filed Mar. 12, 1993, now abandoned, the teachings of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

The leaching of heavy metals from heavy metal bearing wastes has long been of concern to environmental regulators and waste producers. Under the Resource Conservation and Recovery Act, solid waste is classified by the U.S. Environmental Protection Agency (EPA) as hazardous waste if excessive amounts of heavy metals leach from the waste when tested according to the Toxicity Characteristic Leaching procedure (TCLP). In addition, several state governments require that heavy metal bearing wastes, having higher leaching levels, be directed to hazardous waste landfills. Disposal of waste at hazardous waste landfills is typically more expensive than disposal at non-hazardous waste facilities.

To reduce the expenses associated with the landfill disposal of heavy metal leachable waste, particularly lead bearing wastes, various methods to control heavy metal leaching have been developed. These methods include the treatment of lead bearing waste with, for example, phosphates, sulfides, calcium salts, metal oxides, vermiculite, aluminosilicates or portland cement. However, due to the mixing equipment and/or chemicals required, these methods are often expensive to perform. Additionally, some of these methods use chemicals, such as ferric chloride which, in the amounts used, are very corrosive to waste generation and/or treatment process equipment. Furthermore, some methods for reducing lead leaching can result in the formation of potential carcinogens, such as lead phosphate.

Thus, a need exists for means of reducing lead leaching, from lead bearing waste, which are less expensive and less damaging to equipment, and which do not form carcinogenic products.

SUMMARY OF THE INVENTION

The present invention relates to a method for reducing the leaching of lead from a lead bearing waste. The method includes contacting the waste with a water soluble phosphate and a complexing agent, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in the waste, thereby reducing the leaching of lead from the waste as determined by a leach test performed on the waste.

This invention has the advantages of reducing the leachability of lead from lead bearing waste, under leach test conditions, at a lower price and with lesser amounts of phosphate and complexing agent. This invention has the additional advantage of reducing the corrosion, resulting from waste stabilization, of waste production and processing equipment.

DETAILED DESCRIPTION OF THE INVENTION

Waste stabilization is herein defined as reducing the leaching of lead from a lead bearing waste, as determined by performing a suitable leach test on the waste. Wastes suitable for stabilization, according to the method of invention,

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typically include solids in waste streams and waste piles. In a waste stream, the solid waste can optionally be entrained in a liquid or a gas. Examples of lead bearing wastes which can be stabilized include wastes from auto shredders' fluff, wire chop, electroplating processes, arc dust collectors, cupola metal furnaces, sand blasting, and sewage sludge drying beds. Additional examples of wastes suitable for stabilization include residues and products of the combustion, or partial combustion, of medical waste, commercial waste, industrial waste, sewage sludge and solid municipal waste. This method can also be used to stabilize foundry sand.

The lead, in the lead bearing waste to be stabilized, can be in elemental form and/or cationic form. Lead bearing waste can contain up to about 100 ppm, or more, of leachable lead. However, leachable lead levels, in wastes to be stabilized, are more typically between about 5 ppm to about 20 ppm.

Leach test conditions, as defined herein, include the conditions to which a waste is subjected during acetic acid leaching, citric acid leaching, other chelating leaching methods or extraction leaching. Suitable acetic acid leach tests include the Toxicity Characteristic Leaching procedure (TCLP), which is described by the EPA in the USEPA SW-846 Manual. Briefly, in a TCLP test, 100 grams of waste are stirred with 2 liters of dilute acetic acid for a period of 18 hours. The dilution of the acetic acid is 5.7 mLs of concentrated acetic acid per liter of water. Leachable lead, contained in the waste, then complexes with acetate anions to form lead acetate. A TCLP result of 5 ppm lead will result in the classification of the waste as hazardous waste.

Suitable citric acid leach tests include the California Waste Extraction Test (WET), which is described in Title 22, Section 66700, "Environmental Health" of the California Health and Safety Code. Briefly, in a WET test, 50 grams of waste are tumbled in a 1000 mL tumbler with 500 grams of sodium citrate solution for a period of 48 hours. Leachable lead, contained in the waste, then complexes with citrate anions to form lead citrate. The concentration of leached lead is then analyzed by Inductively-Coupled Plasma (ICP) after filtration of a 100 mL aliquot from the tumbler through a 45 micron glass bead filter. A WET result of ≥ 5 ppm lead will result in the classification of the waste as hazardous waste.

In this method for stabilizing lead bearing wastes, a suitable waste is contacted, under alkaline or neutral pH conditions, with a water soluble phosphate and a complexing agent. The complexing agent is typically at least slightly water soluble. When contacted with a phosphate and a complexing agent, lead in the waste forms a lead product, typically a mineral, or complex, which is less soluble than the lead originally in the waste, particularly under leach test conditions. For example, the minerals plumbogummite and chloropyromorphite are formed by contacting lead with Al_2O_3 or Al_2O_3 and chloride ions.

Examples of suitable water soluble phosphates include phosphoric acids, salts of phosphoric acids, P_2O_5 , phosphate rock, combinations thereof and compositions containing one or more non-phosphate components in addition to phosphoric acid(s), phosphoric acid salt(s) and/or P_2O_5 . Examples of such suitable compositions, containing one or more non-phosphate components, include "TRIPLE SUPER PHOSPHATE" fertilizer, which contains P_2O_5 , and phosphoric acid co-product solution resulting from the chemical polishing, or finishing, of aluminum, which includes phosphoric acid and typically nitric acid and/or sulfuric acid. Suitable phosphoric acids include orthophosphoric acid,

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hypophosphoric acid, metaphosphoric acid and pyrophosphoric acid. Salts of phosphoric acids include, for instance, monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.

In one embodiment, suitable complexing agents contain a multivalent metal cation component. The multivalent cation component is typically at least slightly water soluble. Suitable multivalent metal cation components contain, for instance, iron (II), iron (III), aluminum (III) or combinations thereof. Examples of suitable multivalent metal cation components include $\text{Fe}(\text{NO}_3)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, Al_2O_3 , aluminosilicate and combinations thereof.

In an alternate embodiment, suitable complexing agents contain a chloride component which is contained in an aqueous solution or is in the form of a solid water soluble salt. An example of a suitable chloride component is table salt.

The amounts of water soluble phosphate and complexing agent used, according to the method of invention, depend upon various factors, such as the type of waste being stabilized, chemical makeup of the waste, waste porosity, waste cohesiveness, the amount of waste, the concentration of lead within the waste, whether the waste is in a waste stream or a waste pile, and waste treatment objectives, such as the desired final concentration of leachable lead. The amounts of phosphate and complexing agent needed to treat a specific waste can be readily determined by one of ordinary skill in the art through performing one or more leaching tests, such as TCLP or WET, on a sample of the waste.

Typically, the minimum concentrations of phosphate and complexing agent in a treated lead bearing waste, which are needed to stabilize said waste, are about 0.1 wt. % phosphate and about 0.01 wt. % complexing agent.

The stabilization of lead bearing wastes, with various phosphates and complexing agents, is further described in the Example.

It is understood that the phosphate and the complexing agent can be added to the waste either separately, concurrently, in combination, sequentially, intermittently, or in any other sequence or order. It is also understood that the phosphate and/or complexing agent can be added to the waste as solids, in aqueous solution or in a slurry. Furthermore, the phosphate and complexing agent can be contacted with the waste without mixing with the waste, or optionally, with mixing.

In this method, the phosphate and complexing agent can be applied during waste generation, applied to waste contained in a waste stream and/or applied to waste stored in a waste pile. In one embodiment, a phosphate and complexing agent are added to the source of a lead bearing waste prior to generating said lead bearing waste. For example, phosphate and complexing agent can be sprayed, coated, added, mixed or otherwise contacted with copper wire insulation before chopping the copper wire, thereby producing a stabilized lead bearing waste.

In another embodiment, phosphate and complexing agent are coated onto equipment which produces the waste. For example, phosphate and complexing agent can be sprayed, coated or otherwise contacted with wire chopping equipment, prior to, or during operation.

In yet another embodiment, phosphate and complexing agent are contacted with waste contained in a waste stream, typically without restricting the free flow of the waste stream. For example, phosphate and complexing agent can

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be directed onto or into waste in a free flowing waste stream by injection, spraying, coating or other suitable means. Alternatively, phosphate and complexing agent can be coated onto equipment which directs and/or transports waste

5 in a waste stream. For example, phosphate and complexing agent can be sprayed, coated or otherwise contacted with equipment for conveying wire chop waste, such as a screw conveyor, prior to or during equipment operation. Further, for incinerator units, a phosphate and complexing agent can be sprayed, coated or otherwise contacted with gas/solid separators, for separating solids from combustion gases, such as cyclone separators or vortex separators, thereby treating the solid waste while separating the solid waste from the gaseous waste product.

10 In a further embodiment, phosphate and complexing agent can be contacted with waste contained in a waste pile. Typically, the phosphate and complexing agent are added to the surface of the waste pile. Optionally, the phosphate and the complexing agent are directed into the waste pile. 15 Suitable means for directing the phosphate and complexing agent into the waste pile include, for instance, tilling and/or irrigation with surface or subsurface water sprays or water injection. If mixing through tilling, the phosphate and complexing agent are usually mixed into the waste pile to a depth 20 of about one to three feet.

25 The invention will now be further and more specifically described by the following example.

EXAMPLE

Reduction of Lead Leaching From Wastes

Lead bearing wastes were treated with various amounts of several phosphates and/or complexing agents to evaluate the effect of treatment upon the lead leachability of the wastes. The wastes treated included copper wire insulation (CWI) from wire chop processes, bottom ash (BA) from a refuse-to-energy facility, flyash scrubber residue (FASR), collected from air pollution control devices as a mixture of air entrained flyash and residual scrubbing products from CaO injection, and lead contaminated soil (Pb soil).

30 The phosphates used included technical grade phosphoric acid (75 wt% H_3PO_4 and 25 wt% H_2O , hereinafter “ gH_3PO_4 ”), the dry fertilizer “TRIPLE SUPER PHOSPHATE” (TSP), containing 18 wt. % nitrogen and 46 wt. % P_2O_5 , purchased from Solutions, Inc. (Franklin, Mass.) and phosphoric acid co-product solution (COP), resulting from chemical polishing of aluminum and consisting essentially of 35–37 wt. % H_3PO_4 , 25–27 wt. % P_2O_5 , 5–8 Wt. % H_2SO_4 , 1–2 wt. % dissolved aluminum and 0.5–0.7 wt. % HNO_3 . COP was also purchased from Solutions, Inc. (Franklin, MA).

35 The complexing agents used consisted of an aqueous solution $\text{Fe}(\text{NO}_3)_3$ containing 10.25 wt. % Fe(III), aqueous $\text{Fe}_2(\text{SO}_4)_3$ solution containing approximately 10 wt. % Fe(III), 30 wt. % FeCl_3 aqueous solution, “MORTON'S TABLE SALT” containing 1 wt. % NaCl and silicoalumina, “LIQUID ALUMINUM SULFATE”, an aluminum sulfate aqueous solution purchased from Holland Company Inc. (Adams, Mass.), Al_2O_3 and milled bauxite, containing 74.2 wt. % Al_2O_3 and 7.6 wt. % Fe_2O_3 .

40 Following mixing with the phosphate and/or co agent, each waste sample, and each waste sample control, was tested for lead leachability utilizing the EPA's acetate TCLP test. The leach tests results obtained are shown in the following table:

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Waste	Post-Treatment Waste Composition (by weight percent)	Pb Leach (ppm)
CWI	Untreated CWI (CWI control)	24.30
CWI	99% CWI and 1.0% H_3PO_4	19.00
CWI	97% CWI and 3.0% H_3PO_4	0.12
CWI	95% CWI and 5% TSP	0.17
CWI	99% CWI and 1.0% $\text{Fe}_2(\text{SO}_4)_3$	3.70
CWI	99% CWI, 0.5% H_3PO_4 & 0.5% FeCl_3	<0.05
CWI	98.5% CWI, 1.0% H_3PO_4 & 0.5% FeCl_3	<0.05
CWI	97.75% CWI, 2.0% H_3PO_4 & 0.25% $\text{Fe}(\text{NO}_3)_3$	<0.05
CWI	97.25% CWI, 2.5% H_3PO_4 & 0.25% $\text{Fe}(\text{NO}_3)_3$	0.06
CWI	98% CWI, 1.0% H_3PO_4 & 1.0% NaCl	2.30
CWI	98.5% CWI, 1.0% H_3PO_4 & 0.5% Al_2O_3	<0.05
CWI	98% CWI, 1.0% H_3PO_4 & 1.0% Bauxite	<0.05
CWI	98% CWI and 2.0% COP	0.20
CWI	98% CWI, 1.5% COP and 0.5% FeCl_3	<0.05
CWI	98% CWI, 0.5% COP, 0.5% $\text{Fe}_2(\text{SO}_4)_3$ and 1.0% H_2O	0.07
CWI	97% CWI, 0.99% H_3PO_4 , 0.03% FeCl_3 , 0.03 $\text{Al}_2(\text{SO}_4)_3$ and 19.5 H_2O	<0.05
CWI	99% CWI, 0.33% H_3PO_4 , 0.01% FeCl_3 , 0.01 $\text{Al}_2(\text{SO}_4)_3$ and 6.5 H_2O	<5.00
BA	Untreated BA (BA Control)	6.30
BA	99.3% BA, 0.2% H_3PO_4 & 0.5% FeCl_3	<0.05
FASR	Untreated FASR (FASR Control)	36.80
FASR	99% FASR, 0.5% H_3PO_4 & 0.5% FeCl_3	1.90
BA/FASR	99% BA/FASR, 0.5% H_3PO_4 & 0.5% FeCl_3	<0.05
Pb Soil		87.00
Pb Soil	97% Pb Soil and 3.0% COP	1.7

The leach test results demonstrated that treatments of lead bearing wastes, with a combination of a phosphate and a complexing agent generally resulted in lower lead leaching level than did treatment of waste with only a phosphate or with a complexing agent.

Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.

The invention claimed is:

1. A method for reducing the leaching of lead from a lead bearing waste, consisting essentially of contacting said waste with a water soluble phosphate and a complexing agent containing Fe(II), Fe(III), Al(III), chloride or combination thereof, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said waste, thereby reducing the leaching of lead from said waste as determined by a leach test performed on said waste.

2. A method for reducing the leaching of lead from a lead bearing waste, consisting essentially of contacting said waste, under alkaline or neutral pH conditions, with a water soluble phosphate and a complexing agent containing Fe(II), Fe(III), Al(III), chloride or combination thereof, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said waste, thereby reducing the leaching of lead from said waste as determined by a leach test performed on said waste.

3. A method of claim 2 wherein said water soluble phosphate comprises a phosphate selected from the group consisting of phosphoric acids, salts of phosphoric acids, P_2O_5 , phosphate rock and combinations thereof.

4. A method of claim 3 wherein said salts of phosphoric acids include monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.

5. A method of claim 2 wherein the complexing agent contains a multivalent metal cation component selected from the group consisting of $\text{Fe}(\text{NO}_3)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 and combinations thereof.

6. A method of claim 2 wherein the complexing agent contains a multivalent metal cation component selected from the group consisting of $\text{Al}_2(\text{SO}_4)_3$, Al_2O_3 , aluminosilicate and combinations thereof.

7. A method of claim 2 wherein the water soluble phosphate and complexing agent are added to the source of the lead bearing waste prior to generating said lead bearing waste.

8. A method of claim 2 wherein the lead bearing waste is contained in a waste stream.

9. A method of claim 8 wherein the water soluble phosphate and complexing agent are contacted with waste stream equipment prior to or during the generation of lead bearing waste.

10. A method of claim 2 wherein the lead bearing waste is contained in a waste pile.

11. A method of claim 10 wherein the lead bearing waste, the water soluble phosphate and the complexing agent are mixed by tilling.

12. A method of claim 2 further comprising the step of contacting water with the lead bearing waste during or after contacting the water soluble phosphate and the complexing agent with said waste.

13. A method of claim 12 further comprising the step of contacting sulfuric acid with said waste.

14. A method for reducing lead leaching from a waste, when said waste is subjected to leach test conditions, consisting essentially of the steps of:

a) contacting said waste with a phosphoric acid solution; and

b) contacting said waste with ferric sulfate whereby a lead product is formed which is less soluble than the lead originally in said waste, thereby reducing the leaching of lead from said waste as determined by a leach test performed on said waste.

15. A method of claim 14 wherein the ferric sulfate is at least partially dissolved in an aqueous solution.

16. A method of claim 15 wherein the phosphoric acid solution contains sulfuric acid.

17. A method of claim 16 wherein the phosphoric acid solution comprises a phosphoric acid waste product resulting from the chemical polishing or finishing of aluminum.

18. A method for reducing the leaching of lead from a lead bearing waste contained in a waste stream, comprising contacting waste stream equipment prior to or during the generation of said lead bearing waste, under alkaline or neutral pH conditions, with a water soluble phosphate and a complexing agent containing Fe(II), Fe(III), Al(III), chloride or combination thereof, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said waste, thereby reducing the leaching of lead from said waste as determined by a leach test performed on said waste.

19. A method for reducing the leaching of lead from a lead bearing waste, comprising contacting said waste with a composition comprising a water soluble phosphate and a complexing agent containing Fe(II), Fe(III), Al(III), chloride or combination thereof, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said waste, thereby reducing the leaching of lead from said waste as determined by a leach test performed on said waste.

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20. A method of claim 19 wherein said water soluble phosphate comprises a phosphate selected from the group consisting of phosphoric acids, salts of phosphoric acids, P₂O₅, phosphate rock and combinations thereof.

21. A method of claim 20 wherein said salts of phosphoric acids include monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof. 5

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22. A method of claim 19 wherein the complexing agent contains a multivalent metal cation component selected from the group consisting of Fe(NO₃)₃, FeSO₄, Fe₂(SO₄)₃, FeCl₃, Al₂(SO₄)₃, Al₂O₃, aluminosilicate and combinations thereof.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,536,899

DATED : July 16, 1996

INVENTOR(S) : Keith E. Forrester

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In column 5, in the table at line 20, change 19.5 to
--1.95%--

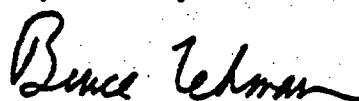
In column 5, in the table at line 22, change 6.5 to
--0.65%.

Signed and Sealed this

Twenty-fifth Day of February, 1997

Attest:

Attesting Officer



BRUCE LEHMAN

Commissioner of Patents and Trademarks



US005722928A

United States Patent [19]
Forrester

[11] Patent Number: **5,722,928**
[45] Date of Patent: ***Mar. 3, 1998**

[54] **STABILIZATION OF LEAD BEARING WASTE**

[76] Inventor: **Keith E. Forrester, P.O. Box 2008, Hampton, N.H. 03843-2008**

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,536,899.

[21] Appl. No.: **683,606**

[22] Filed: **Jul. 15, 1996**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 318,538, Oct. 5, 1994, Pat. No. 5,536,899, which is a continuation-in-part of Ser. No. 38,812, Mar. 12, 1993, abandoned.

[51] Int. Cl⁶ A62D 3/00; B09D 3/00

[52] U.S. Cl. 588/256; 588/260; 588/901

[58] Field of Search 405/128, 129; 588/236, 256, 260, 901

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Attorney, Agent, or Firm—Hamilton, Brook, Smith & Reynolds, P.C.

[57] **ABSTRACT**

A method is disclosed for reducing the leaching of lead from a lead bearing material or waste. The method includes contacting the material or waste with a water soluble phosphate and a complexing agent, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in the material or waste, thereby reducing the leaching of lead from the material or waste as determined by a leach test performed on the material or waste.

20 Claims, No Drawings

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STABILIZATION OF LEAD BEARING WASTE

RELATED APPLICATIONS

This is a continuation-in-part application of U.S. Ser. No. 08/318,538, filed Oct. 5, 1994, now U.S. Pat. No. 5,536,899, which is a continuation-in-part of U.S. Ser. No. 08/038,812, filed Mar. 12, 1993 (abandoned), the teachings of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

The leaching of heavy metals from heavy metal bearing wastes has long been of concern to environmental regulators and waste producers. Under the Resource Conservation and Recovery Act, solid waste is classified by the U.S. Environmental Protection Agency (EPA) as hazardous waste if excessive amounts of heavy metals leach from the waste when tested according to the Toxicity Characteristic Leaching Procedure (TCLP). In addition, several state governments require that heavy metal bearing wastes, having higher leaching levels, be directed to hazardous waste landfills. Disposal of waste at hazardous waste landfills is typically more expensive than disposal at non-hazardous waste facilities.

To reduce the expenses associated with the landfill disposal of heavy metal leachable waste, particularly lead bearing wastes, various methods to control heavy metal leaching have been developed. These methods include the treatment of lead bearing waste with, for example, phosphates, sulfides, calcium salts, metal oxides, vermiculite, aluminosilicates or portland cement. However, due to the mixing equipment and/or chemicals required, these methods are often expensive to perform. Additionally, some of these methods use chemicals, such as ferric chloride which, in the amounts used, are very corrosive to waste generation and/or treatment process equipment. Furthermore, some methods for reducing lead leaching can result in the formation of potential carcinogens, such as lead phosphate.

Thus, a need exists for means of reducing lead leaching, from lead bearing material or waste, which are less expensive and less damaging to equipment, and which do not form carcinogenic products.

SUMMARY OF THE INVENTION

The present invention relates to a method for reducing the leaching of lead from a lead bearing material or waste. The method includes contacting the material or waste with a water soluble phosphate and a complexing agent, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in the material or waste, thereby reducing the leaching of lead from the material or waste as determined by a leach test performed on the material or waste. Preferably the material or waste is contacted with composition comprising a water soluble phosphate, dissolved aluminum and sulfuric acid and/or nitric acid, which composition is a co-product from the chemical polishing of aluminum.

This invention has the advantages of reducing the leachability of lead from lead bearing material or waste, under leach test conditions, at a lower price and with lesser amounts of phosphate and complexing agent. This invention has the additional advantage of reducing the corrosion, resulting from waste stabilization, of waste production and processing equipment.

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DETAILED DESCRIPTION OF THE INVENTION

Material or waste stabilization is herein defined as reducing the leaching of lead from a lead bearing material or waste, as determined by performing a suitable leach test on the material or waste. It should be recognized that the lead bearing material need not be a waste but can be any material containing lead in which it is desirable to stabilize the lead therein. The material can ultimately become waste. Wastes suitable for stabilization, according to the method of invention, typically include solids in waste streams (i.e., a material in liquid or dry form from industrial processing that is commonly subjected to waste disposal) waste piles and material that will be further processed from one waste form to another. In a waste stream, the solid waste can optionally be entrained in a liquid or a gas. Examples of lead bearing materials and wastes which can be stabilized include material and wastes from auto shredders' fluff, wire chop, electroplating processes, arc dust collectors, cupola metal furnaces, sand blasting, sewage sludge drying beds, lead contaminated soil, sweat furnace and incinerator ash. Additional examples of wastes suitable for stabilization include residues and products of the combustion, or partial combustion, of medical waste, commercial waste, industrial waste, sewage sludge and solid municipal waste. This method can also be used to stabilize foundry sand.

The lead, in the lead bearing material or waste to be stabilized, can be in elemental form and/or cationic form. Lead bearing waste can contain up to about 100 ppm, or more, of leachable lead. However, leachable lead levels, in the material to be stabilized, are more typically between about 5 ppm to about 20 ppm.

Leach test conditions, as defined herein, include the conditions to which a material or waste is subjected during acetic acid leaching, citric acid leaching, other chelating leaching methods or extraction leaching. Suitable acetic acid leach tests include the Toxicity Characteristic Leaching Procedure (TCLP), which is described by the EPA in the USEPA SW-846 Manual. Briefly, in a TCLP test, 100 grams of waste are stirred with 2 liters of dilute acetic acid for a period of 18 hours. The dilution of the acetic acid is 5.7 mLs of concentrated acetic acid per liter of water. Leachable lead, contained in the material or waste, then complexes with acetate anions to form lead acetate. A TCLP result of ≥ 5 ppm lead will result in the classification of the waste as hazardous waste.

Suitable citric acid leach tests include the California Waste Extraction Test (WET), which is described in Title 22, Section 66700, "Environmental Health" of the California Health and Safety Code. Briefly, in a WET test, 50 grams of waste are tumbled in a 1000 mL tumbler with 500 grams of sodium citrate solution for a period of 48 hours. Leachable lead, contained in the waste, then complexes with citrate anions to form lead citrate. The concentration of leached lead is then analyzed by Inductively-Coupled Plasma (ICP) after filtration of a 100 mL aliquot from the tumbler through a 45 micron glass bead filter. A WET result of ≥ 5 ppm lead will result in the classification of the waste as hazardous waste.

In one method for stabilizing lead bearing materials or wastes, a suitable material or waste is contacted, under alkaline or neutral pH conditions, with a water soluble phosphate and a complexing agent. The complexing agent is typically at least slightly water soluble. When contacted with a phosphate and a complexing agent, lead in the material or waste forms a lead product, typically a mineral, or complex,

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which is less soluble than the lead originally in the material or waste, particularly under leach test conditions. For example, the minerals plumbogummite and chloropyromorphite are formed by contacting lead with Al_2O_3 or Al_2O_3 and chloride ions.

Examples of suitable water soluble phosphates include, but are not limited to phosphoric acids, salts of phosphoric acids, P_2O_5 , combinations thereof and compositions containing one or more non-phosphate components in addition to phosphoric acid(s), phosphoric acid salt(s) and/or P_2O_5 . Examples of such suitable compositions, containing one or more non-phosphate components, include "TRIPLE SUPER PHOSPHATE (P_2O_5)" fertilizer, which contains P_2O_5 , and phosphoric acid co-product solution resulting from the chemical polishing or finishing, of aluminum, which includes phosphoric acid and typically nitric acid and/or sulfuric acid. Suitable phosphoric acids include orthophosphoric acid, hypophosphoric acid, metaphosphoric acid and pyrophosphoric acid. Salts of phosphoric acids include, for instance, monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.

In one embodiment, suitable complexing agents contain a multivalent metal cation component. The multivalent cation component is typically at least slightly water soluble. Suitable multivalent metal cation components contain, for instance, iron (II), iron (III), aluminum (III) or combinations thereof. Examples of suitable multivalent metal cation components include $\text{Fe}(\text{NO}_3)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, Al_2O_3 , aluminosilicate and combinations thereof.

In an alternate embodiment, suitable complexing agents contain a chloride component which is contained in an aqueous solution or is in the form of a solid water soluble salt. An example of a suitable chloride component is table salt or sodium chloride.

A solution of phosphoric acid, dissolved aluminum and optionally sulfuric acid and/or nitric acid can be premixed together prior to use. A preferred formulation will contain from about 35 to about 37% phosphoric acid, from about 1 to 2% dissolved aluminum and optionally from about 5 to about 8% sulfuric acid and/or from about 0.5 to about 0.7% nitric acid. The ratio and presence of sulfuric acid and/or nitric acid will depend upon the nature of the process employed for polishing or finishing of aluminum. Such formulations are available as waste phosphate resulting from the chemical polishing or finishing of aluminum. These waste phosphate formulations are also known in the industry as co-product or rinse water from the polishing or finishing of aluminum. These waste solutions comprise all the necessary components (i.e., phosphate and complexing agent) for lead stabilization. Their use on a lead bearing material or waste provides a one step method for in-line or in-situ lead stabilization.

The amounts of water soluble phosphate and complexing agent used, according to the method of invention, depend upon various factors, such as the type of material or waste being stabilized, chemical makeup of the material or waste, porosity, cohesiveness, the amount of waste, the concentration of lead within the waste, whether the waste is in a waste stream or a waste pile, and waste treatment objectives, such as the desired final concentration of leachable lead. The amounts of phosphate and complexing agent needed to treat a specific material or waste can be readily determined by one of ordinary skill in the art through performing one or more leaching tests, such as TCLP or WET, on a sample of the material or waste.

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Typically, the minimum concentrations of phosphate and complexing agent in a treated lead bearing material or waste, which are needed to stabilize said material or waste, are about 0.1 wt. % phosphate and about 0.01 wt. % complexing agent.

The stabilization of lead bearing materials or wastes, with various phosphates and complexing agents, is further described in the Example.

It is understood that the phosphate and the complexing agent can be added to the material or waste either separately, concurrently, in combination, sequentially, intermittently, or in any other sequence or order. It is also understood that the phosphate and/or complexing agent can be added to the material or waste as solids, in aqueous solution or in a slurry. Furthermore, the phosphate and complexing agent can be contacted with the material or waste without mixing, or optionally, with mixing.

In this method, the phosphate and complexing agent can be applied during waste generation, applied to waste contained in a waste stream and/or applied to waste stored in a waste pile. In one embodiment, a phosphate and complexing agent are added to the source of a lead bearing waste prior to generating said lead bearing waste. For example, phosphate and complexing agent can be sprayed, coated, added, mixed or otherwise contacted with copper wire insulation before chopping the copper wire, thereby producing a stabilized lead bearing waste.

In another embodiment, phosphate and complexing agent are coated onto equipment which produces the material or waste. For example, phosphate and complexing agent can be sprayed, coated or otherwise contacted with wire chopping equipment, prior to, or during operation. This enables one to stabilize lead in-situ or in-line.

In yet another embodiment, phosphate and complexing agent are contacted with waste contained in a waste stream, typically without restricting the free flow of the waste stream. For example, phosphate and complexing agent can be directed onto or into waste in a free flowing waste stream by injection, spraying, coating or other suitable means. Alternatively, phosphate and complexing agent can be coated onto equipment which directs and/or transports waste in a waste stream. For example, phosphate and complexing agent can be sprayed, coated or otherwise contacted with equipment for conveying wire chop waste, such as a screw conveyor, prior to or during equipment operation. Further, for incinerator units, a phosphate and complexing agent can be sprayed, coated or otherwise contacted with gas/solid separators, for separating solids from combustion gases, such as cyclone separators or vortex separators, thereby treating the solid waste while separating the solid waste from the gaseous waste product.

In a further embodiment, phosphate and complexing agent can be contacted with waste contained in a waste pile. Typically, the phosphate and complexing agent are added to the surface of the waste pile. Optionally, the phosphate and the complexing agent are directed into the waste pile. Suitable means for directing the phosphate and complexing agent into the waste pile include, for instance, tilling and/or irrigation with surface or subsurface water sprays or water injection. If mixing through tilling, the phosphate and complexing agent are usually mixed into the waste pile to a depth of about one to three feet.

The invention will now be further and more specifically described by the following example.

EXAMPLE

Reduction of Lead Leaching From Wastes

Lead bearing wastes were treated with various amounts of several phosphates and/or complexing agents to evaluate the

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effect of treatment upon the lead leachability of the wastes. The wastes treated included copper wire insulation (CWI) from wire chop processes, bottom ash (BA) from a refuse-to-energy facility, flyash scrubber residue (FASR), collected from air pollution control devices as a mixture of air entrained flyash and residual scrubbing products from CaO injection, and lead contaminated soil (Pb soil).

The phosphates used included technical grade phosphoric acid (75 wt % H_3PO_4 and 25 wt % H_2O , hereinafter " H_3PO_4 "), the dry fertilizer "TRIPLE SUPER PHOSPHATE" (TSP), containing 18 wt % nitrogen and 46 wt % P_2O_5 , purchased from Solutions, Inc. (Franklin, Mass.) and phosphoric acid co-product solution (COP), resulting from chemical polishing of aluminum and consisting essentially of 35-37 wt % H_3PO_4 , 25-27 wt % P_2O_5 , 5-8 wt % H_2SO_4 , 1-2 wt % dissolved aluminum and 0.5-0.7 wt % HNO_3 . COP was also purchased from Solutions, Inc. (Franklin, Mass.).

The complexing agents used consisted of an aqueous solution $Fe(NO_3)_3$ containing 10.25 wt % $Fe(III)$, aqueous $Fe_2(SO_4)_3$ solution containing approximately 10 wt % $Fe(III)$, 30 wt % $FeCl_3$ aqueous solution, "MORTON'S TABLE SALT (NaCl)" containing 1 wt % NaCl and silicoalumina, "LIQUID ALUMINUM SULFATE", an aluminum sulfate aqueous solution purchased from Holland Company Inc. (Adams, Mass.), Al_2O_3 and milled bauxite, containing 74.2 wt % Al_2O_3 and 7.6 wt % Fe_2O_3 .

Following mixing with the phosphate and/or complexing agent, each waste sample, and each waste sample control, was tested for lead leachability utilizing the EPA's acetate TCLP test. The leach tests results obtained are shown in the following table:

Waste	Post-Treatment Waste Composition (by weight percent)	Pb Leach (ppm)
CWI	Untreated CWI (CWI control)	24.30
CWI	99% CWI and 1.0% H_3PO_4	19.00
CWI	97% CWI and 3.0% H_3PO_4	0.12
CWI	95% CWI and 5% TSP	0.17
CWI	99% CWI and 1.0% $Fe_2(SO_4)_3$	3.70
CWI	99% CWI, 0.5% H_3PO_4 & 0.5% $FeCl_3$	<0.05
CWI	98.5% CWI, 1.0% H_3PO_4 & 0.5% $FeCl_3$	<0.05
CWI	97.75% CWI, 2.0% H_3PO_4 & 0.25% $Fe(NO_3)_3$	<0.05
CWI	97.25% CWI, 2.5% H_3PO_4 & 0.25% $Fe(NO_3)_3$	0.06
CWI	98% CWI, 1.0% H_3PO_4 & 1.0% NaCl	2.30
CWI	98.5% CWI, 1.0% H_3PO_4 & 0.5% Al_2O_3	<0.05
CWI	98% CWI, 1.0% H_3PO_4 & 1.0% Bauxite	<0.05
CWI	98% CWI and 2.0% COP	0.20
CWI	98% CWI, 1.5% COP and 0.5% $FeCl_3$	<0.05
CWI	98% CWI, 0.5% COP, 0.5% $Fe_2(SO_4)_3$ and 1.0% H_2O	0.07
CWI	97% CWI, 0.99% H_3PO_4 , 0.03% $FeCl_3$, 0.03 $Al_2(SO_4)_3$ and 1.95 H_2O	<0.05
CWI	99% CWI, 0.33% H_3PO_4 , 0.01% $FeCl_3$, 0.01 $Al_2(SO_4)_3$ and 6.5 H_2O	<0.00
BA	Untreated BA (BA Control)	6.30
BA	99.3% BA, 0.2% H_3PO_4 & 0.5% $FeCl_3$	<0.05
FASR	Untreated FASR (FASR Control)	36.80
FASR	99% FASR, 0.5% H_3PO_4 & 0.5% $FeCl_3$	1.90
BA/FASR	99% BA/FASR, 0.5% H_3PO_4 & 0.5% $FeCl_3$	<0.05
Pb Soil		87.00
Pb Soil	97% Pb Soil and 3.0% COP	1.7

The leach test results demonstrated that treatments of lead bearing wastes, with a combination of a phosphate and a complexing agent generally resulted in lower lead leaching level than did treatment of waste with only a phosphate or with a complexing agent.

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Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.

The invention claimed is:

1. A method for reducing the leaching of lead from a lead bearing material or waste, comprising contacting said waste with a composition comprising a water soluble phosphate, acid selected from the group consisting of sulfuric acid, nitric acid and combinations thereof and a complexing agent containing $Fe(II)$, $Fe(III)$, $Al(III)$, chloride or combination thereof, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said material or waste, thereby reducing the leaching of lead from said material or waste.
2. A method of claim 1 wherein said water soluble phosphate comprises a phosphate selected from the group consisting of phosphoric acids, salts of phosphoric acids, P_2O_5 , phosphate rock and combinations thereof.
3. A method of claim 2 wherein said salts of phosphoric acids include monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.
4. A method of claim 1 wherein the complexing agent contains a multivalent metal cation component is selected from the group consisting of $Fe(NO_3)_3$, $FeSO_4$, $Fe_2(SO_4)_3$, $FeCl_3$ and combinations thereof.
5. A method of claim 1 wherein the complexing agent contains a multivalent metal cation component is selected from the group consisting of $Al_2(SO_4)_3$, Al_2O_3 , aluminosilicate and combinations thereof.
6. A method of claim 1 wherein the composition is added to the source of the lead bearing waste prior to generating said lead bearing waste.
7. A method of claim 1 wherein the lead bearing material or waste is contained in a waste stream.
8. A method of claim 3 wherein the composition is contacted with waste stream equipment prior to or during the generation of lead bearing waste.
9. A method of claim 1 wherein the lead bearing material or waste is contained in a waste pile.
10. A method of claim 9 wherein the lead bearing material or waste and the composition are mixed by tilling.
11. A method of claim 1 further comprising the step of contacting water with the lead bearing material or waste during or after contacting the composition with said material or waste.
12. A method of claim 1 wherein the composition is a phosphoric acid waste product resulting from the chemical polishing or finishing of aluminum.
13. A method for reducing the leaching of lead from a lead bearing material or waste, comprising contacting said material or waste with a composition comprising a water soluble phosphate, acid selected from the group consisting of sulfuric acid, nitric acid and combinations thereof and aluminum dissolved therein, whereby a lead product is formed which is less soluble than the lead originally in said material or waste, thereby reducing the leaching of lead from said

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material or waste as determined by a leach test performed on said material or waste.

14. A method of claim 13 wherein said water soluble phosphate comprises a phosphate selected from the group consisting of phosphoric acids, salts of phosphoric acids, P₂O₅, phosphate rock and combinations thereof.

15. A method of claim 14 wherein said salts of phosphoric acids include monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.

16. A method of claim 13 wherein the composition is added to the source of the lead bearing material or waste prior to generating said lead bearing material or waste.

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17. A method of claim 13 wherein the lead bearing material or waste is contained in a waste stream.

18. A method of claim 14 wherein the composition is contacted with waste stream equipment prior to or during the generation of lead bearing waste.

19. The method of claim 13 wherein the water soluble phosphate is phosphoric acid.

20. A method of claim 13 wherein the composition is a phosphoric acid waste product resulting from the chemical polishing or finishing of aluminum.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,722,928
DATED : March 3, 1998
INVENTOR(S) : Keith E. Forrester

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Claim 5, Col. 6 line 36, delete "is".

Claim 6, Col. 6 lines 40 and 41 after each appearance of "bearing" add --material or--.

Claim 8, Col. 6, line 46 after "bearing" add --material or--.

Claim 18, Col. 8, line 5 after "bearing" add --material or--.

Signed and Sealed this

Fifteenth Day of December, 1998



Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks



US005846178A

United States Patent [19]
Forrester

[11] **Patent Number:** **5,846,178**
[45] **Date of Patent:** **Dec. 8, 1998**

[54] **STABILIZATION OF LEAD BEARING WASTE**

[76] Inventor: **Keith E. Forrester**, 883 Ocean Blvd.,
Hampton, N.H. 03843-2008

[21] Appl. No.: **33,386**

[22] Filed: **Mar. 2, 1998**

Related U.S. Application Data

[63] Continuation of Ser. No. 683,606, Jul. 15, 1996, Pat. No. 5,722,928, which is a continuation-in-part of Ser. No. 318, 538, Oct. 5, 1994, Pat. No. 5,536,899, which is a continuation-in-part of Ser. No. 38,812, Mar. 29, 1993, abandoned.

[51] **Int. Cl.⁶** **A62D 3/00; B09B 3/00**

[52] **U.S. Cl.** **588/256; 588/260; 588/901**

[58] **Field of Search** **405/128, 129;
588/236, 256, 260, 901; 210/912**

[56] **References Cited**

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[57]

ABSTRACT

A method is disclosed for reducing the leaching of lead from a lead bearing material or waste. The method includes contacting the material or waste with a water soluble phosphate and a complexing agent, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in the material or waste, thereby reducing the leaching of lead from the material or waste as determined by a leach test performed on the material or waste.

24 Claims, No Drawings

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STABILIZATION OF LEAD BEARING WASTE

RELATED APPLICATIONS

This is a continuation of U.S. Ser. No. 08/683,606, filed Jul. 15, 1996, (U.S. Pat. No. 5,722,928) which is a continuation-in-part application of U.S. Ser. No. 08/318,538, filed Oct. 5, 1994 (U.S. Pat. No. 5,536,899), which is a continuation-in-part of U.S. Ser. No. 08/038,812, filed Mar. 29, 1993 (abandoned), the entire teachings of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

The leaching of heavy metals from heavy metal bearing wastes has long been of concern to environmental regulators and waste producers. Under the Resource Conservation and Recovery Act, solid waste is classified by the U.S. Environmental Protection Agency (EPA) as hazardous waste if excessive amounts of heavy metals leach from the waste when tested according to the Toxicity Characteristic Leaching Procedure (TCLP). In addition, several state governments require that heavy metal bearing wastes, having higher leaching levels, be directed to hazardous waste landfills. Disposal of waste at hazardous waste landfills is typically more expensive than disposal at non-hazardous waste facilities.

To reduce the expenses associated with the landfill disposal of heavy metal leachable waste, particularly lead bearing wastes, various methods to control heavy metal leaching have been developed. These methods include the treatment of lead bearing waste with, for example, phosphates, sulfides, calcium salts, metal oxides, vermiculite, aluminosilicates or portland cement. However, due to the mixing equipment and/or chemicals required, these methods are often expensive to perform. Additionally, some of these methods use chemicals, such as ferric chloride which, in the amounts used, are very corrosive to waste generation and/or treatment process equipment. Furthermore, some methods for reducing lead leaching can result in the formation of potential carcinogens, such as lead phosphate.

Thus, a need exists for means of reducing lead leaching, from lead bearing material or waste, which are less expensive and less damaging to equipment, and which do not form carcinogenic products.

SUMMARY OF THE INVENTION

The present invention relates to a method for reducing the leaching of lead from a lead bearing material or waste. The method includes contacting the material or waste with a water soluble phosphate and a complexing agent, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in the material or waste, thereby reducing the leaching of lead from the material or waste as determined by a leach test performed on the material or waste. Preferably the material or waste is contacted with composition comprising a water soluble phosphate, dissolved aluminum and sulfuric acid and/or nitric acid, which composition is a co-product from the chemical polishing of aluminum.

This invention has the advantages of reducing the leachability of lead from lead bearing material or waste, under leach test conditions, at a lower price and with lesser amounts of phosphate and completing agent. This invention has the additional advantage of reducing the corrosion,

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resulting from waste stabilization, of waste production and processing equipment.

DETAILED DESCRIPTION OF THE INVENTION

Material or waste stabilization is herein defined as reducing the leaching of lead from a lead bearing material or waste, as determined by performing a suitable leach test on the material or waste. It should be recognized that the lead bearing material need not be a waste but can be any material containing lead in which it is desirable to stabilize the lead therein. The material can ultimately become waste. Wastes suitable for stabilization, according to the method of invention, typically include solids in waste streams (i.e., a material in liquid or dry form from industrial processing that is commonly subjected to waste disposal), waste piles and material that will be further processed from one waste form to another. In a waste stream, the solid waste can optionally be entrained in a liquid or a gas. Examples of lead bearing materials and wastes which can be stabilized include material and wastes from auto shredders' fluff, wire chop, electroplating processes, arc dust collectors, cupola metal furnaces, sand blasting, sewage sludge drying beds, lead contaminated soil, sweat furnace and incinerator ash. Additional examples of wastes suitable for stabilization include residues and products of the combustion, or partial combustion, of medical waste, commercial waste, industrial waste, sewage sludge and solid municipal waste. This method can also be used to stabilize foundry sand.

The lead, in the lead bearing material or waste to be stabilized, can be in elemental form and/or cationic form. Lead bearing waste can contain up to about 100 ppm, or more, of leachable lead. However, leachable lead levels, in the material to be stabilized, are more typically between about 5 ppm to about 20 ppm.

Leach test conditions, as defined herein, include the conditions to which a material or waste is subjected during acetic acid leaching, citric acid leaching, other chelating leaching methods or extraction leaching. Suitable acetic acid leach tests include the Toxicity Characteristic Leaching Procedure (TCLP), which is described by the EPA in the USEPA SW-84 Manual. Briefly, in a TCLP test, 100 grams of waste are stirred with 2 liters of dilute acetic acid for a period of 18 hours. The dilution of the acetic acid is 5.7 mLs of concentrated acetic acid per liter of water. Leachable lead, contained in the material or waste, then complexes with acetate anions to form lead acetate. A TCLP result of ≥ 5 ppm lead will result in the classification of the waste as hazardous waste.

Suitable citric acid leach tests include the California Waste Extraction Test (WET), which is described in Title 22, Section 66700, "Environmental Health" of the *California Health and Safety Code*. Briefly, in a WET test, 50 grams of waste are tumbled in a 1000 mL tumbler with 500 grams of sodium citrate solution for a period of 48 hours. Leachable lead, contained in the waste, then complexes with citrate anions to form lead citrate. The concentration of leached lead is then analyzed by Inductively-Coupled Plasma (ICP) after filtration of a 100 mL aliquot from the tumbler through a 45 micron glass bead filter. A WET result of ≥ 5 ppm lead will result in the classification of the waste as hazardous waste.

In one method for stabilizing lead bearing materials or wastes, a suitable material or waste is contacted, under alkaline or neutral pH conditions, with a water soluble phosphate and a complexing agent. The complexing agent is

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typically at least slightly water soluble. When contacted with a phosphate and a complexing agent, lead in the material or waste forms a lead product, typically a mineral, or complex, which is less soluble than the lead originally in the material or waste, particularly under leach test conditions. For example, the minerals plumbogummite and chloropyromorphite are formed by contacting lead with Al_2O_3 or Al_2O_3 and chloride ions.

Examples of suitable water soluble phosphates include, but are not limited to phosphoric acids, salts of phosphoric acids, P_2O_5 , combinations thereof and compositions containing one or more non-phosphate components in addition to phosphoric acid(s), phosphoric acid salt(s) and/or P_2O_5 . Examples of such suitable compositions, containing one or more non-phosphate components, include "TRIPLE SUPER PHOSPHATE (P_2O_5)" fertilizer, which contains P_2O_5 , and phosphoric acid co-product solution resulting from the chemical polishing or finishing of aluminum, which includes phosphoric acid and typically nitric acid and/or sulfuric acid. Suitable phosphoric acids include orthophosphoric acid, hypophosphoric acid, metaphosphoric acid and pyrophosphoric acid. Salts of phosphoric acids include, for instance, monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.

In one embodiment, suitable complexing agents contain a multivalent metal cation component. The multivalent cation component is typically at least slightly water soluble. Suitable multivalent metal cation components contain, for instance, iron (II), iron (III), aluminum (III) or combinations thereof. Examples of suitable multivalent metal cation components include $\text{Fe}(\text{NO}_3)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, Al_2O_3 , aluminosilicate and combinations thereof.

In an alternate embodiment, suitable complexing agents contain a chloride component which is contained in an aqueous solution or is in the form of a solid water soluble salt. An example of a suitable chloride component is table salt or sodium chloride.

A solution of phosphoric acid, dissolved aluminum and optionally sulfuric acid and/or nitric acid can be premixed together prior to use. A preferred formulation will contain from about 35 to about 37% phosphoric acid, from about 1 to 2% dissolved aluminum and optionally from about 5 to about 8% sulfuric acid and/or from about 0.5 to about 0.7% nitric acid. The ratio and presence of sulfuric acid and/or nitric acid will depend upon the nature of the process employed for polishing or finishing of aluminum. Such formulations are available as waste phosphate resulting from the chemical polishing or finishing of aluminum. These waste phosphate formulations are also known in the industry as co-product or rinse water from the polishing or finishing of aluminum. These waste solutions comprise all the necessary components (i.e., phosphate and complexing agent) for lead stabilization. Their use on a lead bearing material or waste provides a one step method for in-line or in-situ lead stabilization.

The amounts of water soluble phosphate and complexing agent used, according to the method of invention, depend upon various factors, such as the type of material or waste being stabilized, chemical makeup of the material or waste, porosity, cohesiveness, the amount of waste, the concentration of lead within the waste, whether the waste is in a waste stream or a waste pile, and waste treatment objectives, such as the desired final concentration of leachable lead. The amounts of phosphate and complexing agent needed to treat a specific material or waste can be readily determined by one

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of ordinary skill in the art through performing one or more leaching tests, such as TCLP or WET, on a sample of the material or waste.

Typically, the minimum concentrations of phosphate and complexing agent in a treated lead bearing material or waste, which are needed to stabilize said material or waste, are about 0.1 wt. % phosphate and about 0.01 wt. % complexing agent.

The stabilization of lead bearing materials or wastes, with various phosphates and complexing agents, is further described in the Example.

It is understood that the phosphate and the complexing agent can be added to the material or waste either separately, concurrently, in combination, sequentially, intermittently, or in any other sequence or order. It is also understood that the phosphate and/or complexing agent can be added to the material or waste as solids, in aqueous solution or in a slurry. Furthermore, the phosphate and complexing agent can be contacted with the material or waste without mixing, or optionally, with mixing.

In this method, the phosphate and complexing agent can be applied during waste generation, applied to waste contained in a waste stream and/or applied to waste stored in a waste pile. In one embodiment, a phosphate and complexing agent are added to the source of a lead bearing waste prior to generating said lead bearing waste. For example, phosphate and complexing agent can be sprayed, coated, added, mixed or otherwise contacted with copper wire insulation before chopping the copper wire, thereby producing a stabilized lead bearing waste.

In another embodiment, phosphate and complexing agent are coated onto equipment which produces the material or waste. For example, phosphate and complexing agent can be sprayed, coated or otherwise contacted with wire chopping equipment, prior to, or during operation. This enables one to stabilize lead in-situ or in-line.

In yet another embodiment, phosphate and complexing agent are contacted with waste contained in a waste stream, typically without restricting the free flow of the waste stream. For example, phosphate and complexing agent can be directed onto or into waste in a free flowing waste stream by injection, spraying, coating or other suitable means. Alternatively, phosphate and complexing agent can be coated onto equipment which directs and/or transports waste in a waste stream. For example, phosphate and complexing agent can be sprayed, coated or otherwise contacted with equipment for conveying wire chop waste, such as a screw conveyor, prior to or during equipment operation. Further, for incinerator units, a phosphate and complexing agent can be sprayed, coated or otherwise contacted with gas/solid separators, for separating solids from combustion gases, such as cyclone separators or vortex separators, thereby treating the solid waste while separating the solid waste from the gaseous waste product.

In a further embodiment, phosphate and complexing agent can be contacted with waste contained in a waste pile. Typically, the phosphate and complexing agent are added to the surface of the waste pile. Optionally, the phosphate and the complexing agent are directed into the waste pile. Suitable means for directing the phosphate and complexing agent into the waste pile include, for instance, tilling and/or irrigation with surface or subsurface water sprays or water injection. If mixing through tilling, the phosphate and complexing agent are usually mixed into the waste pile to a depth of about one to three feet.

The invention will now be further and more specifically described by the following example.

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EXAMPLE

Reduction of Lead Leaching from Wastes

Lead bearing wastes were treated with various amounts of several phosphates and/or complexing agents to evaluate the effect of treatment upon the lead leachability of the wastes. The wastes treated included copper wire insulation (CWI) from wire chop processes, bottom ash (BA) from a refuse-to-energy facility, flyash scrubber residue (FASR), collected from air pollution control devices as a mixture of air entrained flyash and residual scrubbing products from CaO injection, and lead contaminated soil (Pb soil).

The phosphates used included technical grade phosphoric acid (75 wt % H₃PO₄ and 25 wt % H₂O, hereinafter "H₃PO₄"), the dry fertilizer "TRIPLE SUPER PHOSPHATE (TSP)", containing 18 wt % nitrogen and 46 wt % P₂O₅, purchased from Solutions, Inc. (Franklin, Mass.) and phosphoric acid co-product solution (COP), resulting from chemical polishing of aluminum and consisting essentially of 35-37 wt % H₃PO₄, 25-27 wt % P₂O₅, 5-8 wt % H₂SO₄, 1-wt % dissolved aluminum and 0.5-0.7 wt % HNO₃. COP was also purchased from Solutions, Inc. (Franklin, Mass.).

The complexing agents used consisted of an aqueous solution Fe(NO₃)₃ containing 10.25 wt % Fe(III), aqueous Fe₂(SO₄)₃ solution containing approximately 10 wt % Fe(III), 30 wt % FeCl₃ aqueous solution, "MORTON'S TABLE SALT (NaCl)" containing 1 wt % NaCl and silicoalumina, "LIQUID ALUMINUM SULFATE", an aluminum sulfate aqueous solution purchased from Holland Company Inc. (Adams, Mass.), Al₂O₃ and milled bauxite, containing 74.2 wt % Al₂O₃ and 7.6 wt % Fe₂O₃.

Following mixing with the phosphate and/or complexing agent, each waste sample, and each waste sample control, was tested for lead leachability utilizing the EPA's acetate TCLP test. The leach tests results obtained are shown in the following table:

Waste	Post-Treatment Waste Composition (by weight percent)	Pb Leach (ppm)
CWI	Untreated CWI (CWI control)	24.30
CWI	99% CWI and 1.0% H ₃ PO ₄	19.09
CWI	97% CWI and 3.0% H ₃ PO ₄	0.12
CWI	95% CWI and 5% TSP	0.17
CWI	99% CWI and 1.0% Fe ₂ (SO ₄) ₃	3.70
CWI	99% CWI, 0.5% H ₃ PO ₄ & 0.5% FeCl ₃	<0.05
CWI	98.5% CWI, 1.0% H ₃ PO ₄ & 0.5% FeCl ₃	<0.05
CWI	97.75% CWI, 2.0% H ₃ PO ₄ & 0.25% Fe(NO ₃) ₃	<0.05
CWI	97.25% CWI, 2.5% H ₃ PO ₄ & 0.25% Fe(NO ₃) ₃	0.06
CWI	98% CWI, 1.0% H ₃ PO ₄ & 1.0% NaCl	2.30
CWI	98.5% CWI, 1.0% H ₃ PO ₄ & 0.5% Al ₂ O ₃	<0.05
CWI	98% CWI, 1.0% H ₃ PO ₄ & 1.0% Bauxite	<0.05
CWI	98% CWI and 2.0% COP	0.20
CWI	98% CWI, 1.5% COP and 0.5% FeCl ₃	<0.05
CWI	98% CWI, 0.5% COP, 0.5% Fe ₂ (SO ₄) ₃ and 1.0% H ₂ O	0.07
CWI	97% CWI, 0.99% H ₃ PO ₄ , 0.03% FeCl ₃ , 0.03 Al ₂ (SO ₄) ₃ and 19.5 H ₂ O	<0.05
CWI	99% CWI, 0.33% H ₃ PO ₄ , 0.01% FeCl ₃ , 0.01 Al ₂ (SO ₄) ₃ and 6.5 H ₂ O	<5.00
BA	Untreated BA (BA Control)	6.30
BA	99.3% BA, 0.2% H ₃ PO ₄ & 0.5% FeCl ₃	<0.05
FASR	Untreated FASR (FASR Control)	36.80
FASR	99% FASR, 0.5% H ₃ PO ₄ & 0.5% FeCl ₃	1.90
BA/FASR	99% BA/FASR, 0.5% H ₃ PO ₄ & 0.5% FeCl ₃	<0.05
Pb Soil		87.00
Pb Soil	97% Pb Soil and 3.0% COP	1.7

The leach test results demonstrated that treatments of lead bearing wastes, with a combination of a phosphate and a

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complexing agent generally resulted in lower lead leaching level than did treatment of waste with only a phosphate or with a complexing agent.

EQUIVALENTS

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.

The invention claimed is:

1. A method for reducing the leaching of lead from a lead bearing material or waste, comprising contacting said material or waste with a water soluble phosphate and acid selected from the group consisting of sulfuric acid, nitric acid and combinations thereof, in the presence of a complexing agent containing Fe(II), Fe(III), Al(III), chloride or combination thereof, wherein the complexing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said material or waste, thereby reducing the leaching of lead from said material or waste as determined by a leach test performed on said material or waste.

2. The method of claim 1 wherein said water soluble phosphate comprises a phosphate selected from the group consisting of phosphoric acids, salts of phosphoric acids, P₂O₅, phosphate rock and combinations thereof.

3. The method of claim 2 wherein said salts of phosphoric acids include monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof.

4. The method of claim 1 wherein the complexing agent contains a multivalent metal cation component selected from the group consisting of Fe(NO₃)₃, FeSO₄, Fe₂(SO₄)₃, FeCl₃ and combinations thereof.

5. The method of claim 1 wherein the complexing agent contains a multivalent metal cation component selected from the group consisting of Al₂(SO₄)₃, Al₂O₃, aluminosilicate and combinations thereof.

6. The method of claim 1 wherein the phosphate and acid are added to the source of the lead bearing material or waste prior to generating said lead bearing material or waste.

7. The method of claim 1 wherein the lead bearing material or waste is contained in a waste stream.

8. The method of claim 3 wherein the phosphate and acid are contacted with waste stream equipment prior to or during the generation of lead bearing material or waste.

9. The method of claim 1 wherein the lead bearing material or waste is contained in a waste pile.

10. The method of claim 9 wherein the lead bearing material or waste and the phosphate and acid are mixed by tilling.

11. The method of claim 1 further comprising the step of contacting water with the lead bearing material or waste during or after contacting the phosphate and acid with said material or waste.

12. The method of claim 1 wherein waste phosphoric acid solution resulting from the chemical polishing or finishing of aluminum is used as the source of phosphate and acid.

13. A method for reducing the leaching of lead from a lead bearing material or waste, comprising contacting said material or waste with a composition comprising a water soluble phosphate and acid selected from the group consisting of sulfuric acid, nitric acid and combinations thereof, in the presence of aluminum and/or iron multivalent cationic component, whereby a lead product is formed which is less soluble than the lead originally in said material or waste,

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thereby reducing the leaching of lead from said material or waste as determined by a leach test performed on said material or waste.

14. The method of claim 13 wherein said water soluble phosphate comprises a phosphate selected from the group consisting of phosphoric acids, salts of phosphoric acids, ⁵ P_2O_5 , phosphate rock and combinations thereof.

15. The method of claim 13 wherein the water soluble phosphate is phosphoric acid.

16. The method of claim 14 wherein said salts of phosphoric acids include monoammonium phosphate, diammonium phosphate, disodium hydrogen phosphate, trisodium phosphate and combinations thereof. ¹⁰

17. The method of claim 13 wherein the composition is added to the source of the lead bearing material or waste prior to generating said lead bearing material or waste. ¹⁵

18. The method of claim 13 wherein the lead bearing material or waste is contained in a waste stream.

19. The method of claim 14 wherein the composition is contacted with waste stream equipment prior to or during the generation of lead bearing material or waste. ²⁰

20. The method of claim 13 wherein the composition is a waste phosphoric acid solution comprising a source of

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phosphate and acid resulting from the chemical polishing or finishing of aluminum.

21. The method of claim 13 wherein the iron is derived from a water soluble iron source.

22. The method of claim 21 wherein the water soluble iron source is ferric sulfate.

23. A method for reducing the leaching of lead from lead bearing incinerator ash, comprising contacting said incinerator ash with a water soluble phosphate and acid selected from the group consisting of sulfuric acid, nitric acid and combinations thereof, in the presence of a complexing agent containing Fe(II), Fe(III), Al(III), chloride or combination thereof, wherein the completing agent is at least slightly water soluble, whereby a lead product is formed which is less soluble than the lead originally in said incinerator ash, thereby reducing the leaching of lead from said incinerator ash as determined by a leach test performed on said incinerator ash.

24. The method of claim 23 wherein the water soluble phosphate is phosphoric acid and the acid is sulfuric acid.

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US007530939B2

(12) **United States Patent**
Forrester

(10) **Patent No.:** US 7,530,939 B2
(b5) **Date of Patent:** May 12, 2009

(54) **METHOD FOR STABILIZATION OF HEAVY METALS IN INCINERATOR BOTTOM ASH AND ODOR CONTROL WITH DICALCIUM PHOSPHATE DIHYDRATE POWDER**

(75) Inventor: **Keith Edward Forrester**, Meredith, NH (US)

(73) Assignee: **Keith E. Forrester**, Meredith, NH (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 119 days.

(21) Appl. No.: **11/713,857**

(22) Filed: **Mar. 5, 2007**

(65) **Prior Publication Data**

US 2007/0225541 A1 Sep. 27, 2007

Related U.S. Application Data

(60) Provisional application No. 60/786,035, filed on Mar. 25, 2006.

(51) **Int. Cl.**

B09B 3/00 (2006.01)

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See application file for complete search history.

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(57) **ABSTRACT**

This invention provides a method for stabilization and treatment of heavy metal bearing materials and wastes subject to acid leaching tests or leach conditions and odor limits by addition of acid semi-soluble DiCalcium Phosphate DiHydrate such that the leaching potential is inhibited to desired levels and odors are reduced to desired levels and the material or waste is free flowing, more permeable, less weight and permits immediate handling and disposal or reuse. The resultant material or waste after stabilization is deemed suitable for on-site reuse, off-site reuse or disposal as RCRA non-hazardous waste.

8 Claims, No Drawings

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METHOD FOR STABILIZATION OF HEAVY METALS IN INCINERATOR BOTTOM ASH AND ODOR CONTROL WITH DICALCIUM PHOSPHATE DIHYDRATE POWDER

RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/786,035, filed on Mar. 25, 2006. This patent application incorporates and embodies the above 10

BACKGROUND OF THE INVENTION

Over the past thirty years, the potential and observed dangers of heavy metal bearing materials and waste exposure to humans and the environment and the generation of nuisance odors and from solid waste management facilities has been the basis of extensive regulatory control. The leaching and transport of heavy metals into surface water bodies and groundwater is a grave concern because of the danger that the drinking water supplies and the environment will become contaminated. Heavy metal bearing materials and wastes, such products or waste, paint residues, sludge, plating wastes, sediments, foundry dusts, casting sands, steel mill dusts, shredder residues, wire insulation, refuse incinerator flyash, incinerator bottom ash, incinerator combined ash, scrubber residues from air pollution control devices such as cyclones, electrostatic precipitators and bag-house filter bags, may be deemed hazardous by the United States Environmental Protection Agency (U.S. EPA) pursuant to 40 C.F.R. Part 261 if containing certain soluble heavy metals above regulatory limits. Any solid waste can be defined as hazardous either because it is "listed" in 40 C.F.R., Part 261 Subpart D or because it exhibits one or more of the characteristics of a 35 hazardous waste as defined at Part 261, Subpart C. These characteristics are: (1) ignitability, (2) corrosivity, (3) reactivity, and (4) toxicity as tested under the Toxicity Characteristic Leaching Procedure (TCLP). Heavy metal bearing materials and wastes can also be regulated under state and federal groundwater and surface water protection standards, which set total and leachable limits for heavy metals often lower than the TCLP criteria, as the wastes and materials are not in a lined landfill and exposed to direct groundwater, drinking 50 water, storm waters and surface water bodies. The odor produced during management or stabilization of these wastes and materials, such as from refuse incinerator ash residues and operations that process ash residues, can become problematic for the operators of such facilities, as many waste generation and stabilization operations are nearby industrial, commercial and/or residential settings. Odor emissions are regulated mostly under local ordinance rules of nuisance and some countries under federal and/or state air quality regulations.

40 C.F.R., Part 261.24(a), contains a list of contaminants and their associated maximum allowable concentrations. The inorganic list includes As, Ag, Ba, Cd, Cr, Pb, Hg, and Se. If a contaminant exceeds its maximum allowable concentration, when tested using TCLP analysis as specified at 40 C.F.R. 55 Part 261 Appendix 2, then the material is classified as hazardous. The TCLP test uses a dilute acetic acid either in de-ionized water (TCLP fluid 2) or in de-ionized water with a sodium hydroxide buffer (TCLP fluid 1). Both extracts attempt to simulate the leachate character from a decomposing trash landfill in which the hazardous waste being tested for is assumed to be disposed of in, and thus subject to the acetic acid leaching condition. Waste containing leachable

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heavy metals is currently classified as hazardous waste due to the toxicity characteristic, if the level of TCLP analysis is above 0.2 to 100 milligrams per liter (mg/L) or parts per millions (ppm) for defined metals. The TCLP test is designed 5 to simulate a worst-case leaching situation, i.e., leachate which would typically be found in the interior of an actively degrading municipal landfill. Such landfills normally are slightly acidic with a pH of approximately 5+0.5. Countries outside of the US also use the TCLP test as a measure of leachability such as Taiwan, Philippines, Thailand, and Canada. Thailand also limits solubility of Cu and Zn, as these are metals of concern to Thailand groundwater. Switzerland and most European countries also regulate management of solid wastes by measuring heavy metals and salts as tested by a sequential leaching method using carbonated water simulating acid rainwater. Japan and the United Kingdom use similar carbonated DI water leach tests to measure for landfill leaching potential from heavy metals.

Additionally, U.S. EPA land disposal restrictions prohibit 20 the land disposal of treated hazardous wastes that leach in excess of maximum allowable concentrations upon performance of the TCLP analysis. The land disposal regulations require that hazardous wastes are treated until the heavy metals do not leach at Universal Treatment Standard (UTS) levels 25 from the solid waste at levels above the maximum allowable concentrations prior to placement in a surface impoundment, waste pile, landfill or other land disposal unit as defined in 40 C.F.R. 260.10.

Communities have local ordinances that regulate the generation of odors that would be a public nuisance, and in some cases regulators have established maximum allowable odor index levels. Maximum hourly average and daily average chemical gas and particulate levels have also been established under the US Clean Air Act and Amendments, and by OSHA and NIOSH. Odor Index Tests using varied levels of activated carbon mixed with the subject waste or material and utilizing a panel of people with human olfactory sense is one method of comparing odors. The panel is asked to confirm or deny sense of odor, which is related to the amount of activated carbon used in the subject waste and generates an odor index. The lower the index, the stronger the odor would be encountered. There may exist certain health and environmental release risks from the emission and transfer or diffusion of odor bearing gases, and thus the need to control and reduce such odiferous gases may extend beyond a simple nuisance issue. H₂S gas for example, having a rotten egg odor, is highly toxic and can cause death in humans upon exposure to lower lethal levels at very low duration.

Leach tests subject solid wastes, including sludge, ash, residues, material or soil, to dilute acetic acid leaching (TCLP), buffered citric acid leaching (STLC), distilled water, synthetic rainwater (SPLP, MEP) or carbonated water leaching (Japanese, UK, Swiss, and USEPA SW-924). Synthetic rainwater leach tests are also often used to measure heavy metal solubility and compare such to groundwater and surface water state and federal standards where materials and wastes are either reused on-site or disposed in a manner other than lined landfills.

Suitable acetic acid leach tests include the USEPA SW-846 Manual described Toxicity Characteristic Leaching Procedure (TCLP) and Extraction Procedure Toxicity Test (EP Tox) now used in Canada. Briefly, in a TCLP test, 100 grams of waste are tumbled with 2000 ml of dilute and buffered acetic acid for 18 hours. The extract solution is made up from 5.7 ml of glacial acetic acid and 64.3 ml of 1.0 normal sodium hydroxide up to 1000 ml dilution with reagent water.

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Suitable synthetic acid leach tests include the USEPA SW-846 Manual described Synthetic Precipitant Leaching Procedure (SPLP) and Multiple Extraction Procedure Test (MEP) now used in the US for sites where wastes are reused outside of leachate collected and lined landfills. Briefly, in a SPLP test, 100 grams of waste are tumbled with 2000 ml of dilute nitric and sulfuric acid for 18 hours. The extract solution is made up to pH at near 4.8 simulating acid rainwater East and West of the Mississippi. The MEP is the Multiple Extraction Procedure which uses the TCLP type test for the first extract and followed by 9 cycles of the SPLP, all of which report leachate values, and thus attempt to measure diffusion potential of the waste matrix.

Suitable carbonated water leach tests include the Japanese leach test which tumbles 50 grams of composited waste sample in 500 ml of water for 6 hours held at pH 5.8 to 6.3, followed by centrifuge and 0.45 micron filtration prior to analyses. Another suitable distilled water CO₂ saturated method is the Swiss protocol using 100 grams of cemented waste at 1 cm³ in two (2) sequential water baths of 2000 ml. The concentration of heavy metals and salts are measured for each bath and averaged together before comparison to the Swiss criteria.

Suitable citric acid leach tests include the California Waste Extraction Test (WET), which is described in Title 22, Section 66700, "Environmental Health" of the California Health & Safety Code. Briefly, in a WET test, 50 grams of waste are tumbled in a 1000 ml tumbler with 500 grams of sodium citrate solution for a period of 48 hours. The heavy metal concentration is then analyzed by Inductively-Coupled Plasma (ICP) after filtration of a 100 ml aliquot from the tumbler through a 45 micron glass bead filter.

Suitable odor measure test would be include activated carbon modified samples with comparative olfactory measure of resultant odor by human panel.

Of specific interest and concern regarding the present invention is the leaching of individual heavy metal groups including As, Hg, Cd, Cr, Cu, and Pb and combinations thereof under TCLP, SPLP, MEP, CALWET, acid rainwater and acid rain derived surface water conditions and under regulatory tests which attempt to simulate dilute acid water leaching for determination of hazardousness of incinerator ash residues. In addition, the reduction of odor generation from the handling and stabilization of ash is desired, as the processing and stabilization of incinerator ash is often in close proximity to adjacent industrial, commercial and residential settings. In a specific case, incinerator ash management and stabilization caused strong odors which in turn resulted in complaints to regulators, and thus the subject invention was developed to reduce odors and allow for stabilization.

The present invention provides a method of reducing the leachability of material or waste including the groups As, Hg, Cd, Cr, Cu, and Pb and combinations thereof under TCLP, SPLP, MEP, CALWET, acid rainwater and acid rain derived surface water leaching conditions, and reduce sensible odors generated during such stabilization, with use of dilute acid semi-soluble DiCalcium Phosphate DiHydrate (DCPDH) [CaHPO₄.2H₂O] pulverized "seed" that minimize weight increase of the treated material or waste and permit immediate stabilized matrix management and handling without water application and mixing, without curing requirements and associated double handling required from interim storage piles, and while producing a free-flowing and more permeable stabilized material or waste suitable for excavator or loader loading, truck unloading and land disposal or immediate reuse spreading and compaction. The present invention

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recognizes the use of dilute acids as leaching fluids to which DCPDH will be added, and thus teaches use of a stabilizer that is dilute acid semi-soluble.

Unlike the present invention, prior art has taught stabilization of heavy metals by addition of water soluble or water based physical encapsulation agents, and have failed to recognize the value of stabilizers which are not water soluble or have limited water solubility, yet are semi-soluble or available in dilute acetic acid (TCLP), dilute sulfuric and nitric acid (SPLP/MEP) and dilute citric acid (CALWET), and failed to produce a stabilization process with reduction of odor production. In particular, O'Hara (U.S. Pat. No. 4,737,356) and Forrester (U.S. Pat. Nos. 5,245,114 and 5,430,233) teach the need to add water soluble phosphates to incinerator ash, auto shredder and wire insulation wastes, and incinerator bottom ash, which are at least 5 gm/100 ml water solubility, with the preferred embodiment being 100% water soluble phosphoric acid, and which increases the odors from incinerator ash. Prior art stabilization methods using Portland cement, lime, cement kiln dust, phosphoric acids, and combinations also produce a reduced permeability matrix or solid material form by adding water (by combination or as part of the water soluble agent addition) to the stabilization recipe for a chemical reaction which presents post-stabilization handling and disposal complications, whereas the present invention use of pulverized DCPDH acts to reduce metals solubility without significant reduction of waste permeability, without formation of cement-like non-free flowing material or waste, without curing time, without water hydration and associated material and waste weight increase, without double material and soil handling required for curing stockpiles, thus permitting immediate stabilizer material or waste handling, loading, disposal or reuse. The pulverized DCPDH semi-soluble seed stabilization method operates on the basic principle that sufficient wet dilute acid environment contact and mixing between the material or waste and DCPDH will occur within the TCLP, SPLP, MEP or CALWET extraction vessel. Although the exact reason for odor reduction is not known at this time, it is postulated that the odors are reduced due to the fine powder and neutral nature of DCPDH which acts as an adsorbent of organics and sulfides produced from ash. The extraction method(s) used to predict leaching potential all assume that field material or waste disposal conditions are subject to hydration by acid rainwater or acid leachate and involve some degree of interstitial mixing of heavy metals with the extract fluid over some minimal period of time in a saturated environment, and that such hydration can be simulated by an extract solute addition and mixing period. The DCPDH seed stabilization method thus utilizes the regulatory extraction procedure to allow for post-stabilized material or waste hydration, mixing and wet chemistry dilute acid environment contact between heavy metals and DCPDH. The extraction tests thus act as dilute acid stirred tank reactors, which provide the opportunity for heavy metals on the surface of materials and waste, and that which diffuses into the acid solution, to have ample opportunity to contact DCPDH seeds that also have surface active and/or soluble mineral formation potentials with the dilute acid soluble and/or available heavy metals. Studies by the inventor found that the lower surface area non-pulverized forms of DCPDH were less effective in reducing heavy metals solubility, which confirmed that the surface area and semi-solubility of the exposed surface area of DCPDH played an important role in the mineral formation potentials. One unique benefit of the dry seed technology is that SPLP, MEP, TCLP and CALWET extract fluid acid soluble and pulverized DCPDH can be applied to waste or material and dry mixed for uniformity in the field, and con-

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sequently test samples of such stabilizers are allowed to freely tumble or mix in the presence of the heavy metals in the extract solution for a given extraction period of time. This non-cemented and non-reacted acid semi-soluble DCPDH pulverized surface mixing greatly improves the wet environment substitution of heavy metals such as Pb, Cd, Cr, Ni, and As into calcium phosphate apatite surfaces. The extraction device effectively puts the heavy metals into solution as well as some DCPDH into solution and remaining DCPDH surfaces into wet contact and thus provides an excellent opportunity for surface substitution, sorption and precipitation of now solution soluble and solution face reactive heavy metals. Under this chemical mechanism, some or all stabilization agents are made available to the solution by the acid solution, and heavy metal ions are made available to the solution which in turn substitute and exchange for calcium on insoluble apatite surfaces and precipitate with stabilization agents in acid solution.

U.S. Pat. No. 5,202,033 describes an in-situ method for decreasing Pb TCLP leaching from solid waste using a combination of solid waste additives and additional pH controlling agents from the source of phosphate, carbonate, and sulfates.

U.S. Pat. No. 5,037,479 discloses a method for treating highly hazardous waste containing unacceptable levels of TCLP Pb such as lead by mixing the solid waste with a buffering agent selected from the group consisting of magnesium oxide, magnesium hydroxide, reactive calcium carbonates and reactive magnesium carbonates with an additional agent which is either an acid or salt containing an anion from the group consisting of Triple Superphosphate (TSP), ammonium phosphate, diammmonium phosphate, phosphoric acid, boric acid and metallic iron.

U.S. Pat. No. 4,889,640 discloses a method and mixture from treating TCLP hazardous lead by mixing the solid waste with an agent selected from the group consisting of reactive calcium carbonate, reactive magnesium carbonate and reactive calcium magnesium carbonate.

U.S. Pat. No. 4,652,381 discloses a process for treating industrial wastewater contaminated with battery plant waste, such as sulfuric acid and heavy metals by treating the waste waster with calcium carbonate, calcium sulfate, calcium hydroxide to complete a separation of the heavy metals. However, this is not for use in a solid waste situation.

Unlike the present invention, however, none of the prior art solutions taught specific dilute acid semi-soluble dry pulverized DCPDH seed stabilization of heavy metal bearing material or waste containing one or more heavy metals while also forming a free-flowing, more permeable stabilized matrix suitable for loading, transport, disposal and reuse without having a cement-like reduced permeability and strength, and without the burden of curing and associated double waste handling, and without reduction of odor. Specifically, prior art has failed to teach the mechanism of acid semi-soluble and pulverized DCPDH seed to allow intentional leaching of heavy metals into the regulatory extraction vessel and subsequent substitution of such metals onto DCPDH surfaces and precipitation and complex formation with a certain acid semi-soluble amount of DCPDH in acid solution.

SUMMARY OF THE INVENTION

The present invention discloses a heavy metal bearing material or waste stabilization method through contact of material or waste with acid semi-soluble DCPDH pulverized seed which complements the material or waste leaching potential and desired free-flowing and more permeable mate-

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rial or waste handling characteristics without hydration, curing and associated additional waste or material interim storage, handling, transport, disposal costs, and provides waste odor reduction. Of specific interest is the disclosure that pulverized DCPDH provides for heavy metal stabilization by surface substitution or by precipitation with acid semi-soluble DCPDH during the regulatory extraction procedure. The DCPDH is provided in dry pulverized chemical form, and thus can be contacted with heavy metal bearing material either prior to waste production such as in-stream at wastewater facilities producing sludge or in-duct prior to air pollution control and ash collection devices or after waste production in material collection devices or waste piles.

It is anticipated that pulverized DCPDH can be used for both RCRA compliance actions such that generated wastes or materials from wastewater facilities, furnaces, incinerators and other facilities do not exceed the TCLP hazardous waste criteria under TCLP or CERCLA (Superfund) response where stabilizers are added to waste piles or storage vessels previously generated. The preferred method of application of pulverized DCPDH would be in-line within the property and facility generating the heavy metal bearing material, and thus allowed under RCRA as a totally enclosed, in-tank or exempt method of TCLP stabilization without the need for a RCRA Part B hazardous waste treatment and storage facility permit.

DETAILED DESCRIPTION

Environmental regulations throughout the world such as those promulgated by the USEPA under CAA, RCRA and CERCLA require heavy metal bearing waste and material producers to manage such materials and wastes in a manner safe to the environment and protective of human health, and reduce nuisance and toxic odor emissions. In response to these regulations, environmental engineers and scientists have developed numerous means to control heavy metals and emissions, mostly through chemical applications which convert the solubility of the material and waste character to a low soluble form, thus passing leach tests and allowing the wastes to be either reused on-site or disposed at local landfills without further and more expensive control means such as hazardous waste disposal landfills or facilities designed to provide metals stabilization, and odor and emissions reduction by air dilution, odor masking agents addition or gas destruction. The primary focus of scientists has been on singular heavy metals such as lead, cadmium, chromium, arsenic and mercury, as these were and continue to be the most significant mass of metals contamination in soils. Materials such as lead paints, incinerator ash, foundry and mill flyash, auto shredder and wire shredding residues and cleanup site wastes such as battery acids and slag wastes from smelters are major lead sources. Recently, however, there exists a demand for control methods of process odor emissions and leaching of various heavy metals such as As, Hg, Cd, Cr, Pb, Cu and combinations thereof in mining waste, wastewater sludge, shredder wastes, wire insulation, incinerator flyash, incinerator bottom ash, incinerator combined ash, foundry dusts, steel mill dusts, and contaminated soils to meet nuisance regulations on odors and TCLP and also SPLP, MEP, DI and other measures intended to measure field condition leaching and/or solubility of the metals under digestion, in a manner which is rapid, low risk to workers, low impact on mechanical process equipment, low cost, avoids interim storage and curing time, and permits on-site or off-site reuse and handling at moisture levels below or at optimum for compaction and handling.

The present invention discloses a heavy metal bearing material or waste stabilization method and odor reduction

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method through contact of material or waste with pulverized DCPDH acid semi-soluble stabilizing agent. The DCPDH found effective is available in dry pulverized form, as well as less effective larger particle size particles, and thus can be contacted with heavy metal bearing material prior to waste generation such as in-stream at wastewater sludge producing plants or in-duct prior to air pollution control and ash collection devices or after waste production in collection devices such as hoppers, dump valves, conveyors, dumpsters or waste piles. The DCPDH is applied dry, thus allowing stabilized material and waste to remain suitable for fill material or loose handling and to remain less permeable thus allowing for transmission of leachate or water flow. The transmission of water flow becomes important an necessary when using the stabilized waste or material as base fill, cover, embankment or engineered fill, thus eliminating damming or leachate production perched water table effects.

The acid semi-soluble pulverized DCPDH dry seed stabilization method reduces the odor from waste and leachability of heavy metal bearing wastes including the groups As, Hg, Cd, Cr, Pb, and Cu and combinations thereof under TCLP, SPLP, MEP, CALWET, DI, rainwater and surface water leaching conditions as well as under regulatory water extraction test conditions as defined by waste control regulations in UK, Thailand, Japan, Switzerland, Germany, Sweden, the Netherlands and under American Nuclear Standards for sequential leaching of wastes, with use of acid semi-soluble dry chemical pulverized DCPDH "seed" to minimize weight increase of the treated waste and permit immediate stabilized matrix management and handling without curing requirements or double handling required for interim storage, and producing a free-flowing and more permeable stabilized material or waste suitable for excavator or loader loading, truck unloading and land disposal or immediate reuse spreading and compaction.

The present invention provides a method of reducing the waste odors and leachability of material or waste including the groups As, Hg, Cd, Cr, Pb, and Cu and combinations thereof under TCLP, SPLP, MEP, CALWET, acid rainwater and acid rain derived surface water leaching conditions, with use of dilute acid semi-soluble DCPDH pulverized seed that minimizes weight increase of the treated material or waste and permit immediate stabilized matrix management and handling without water application and mixing, without curing requirements and associated double handling required from interim storage piles, and while producing a free-flowing and more permeable stabilized material or waste suitable for excavator or loader loading, truck unloading and land disposal or immediate reuse spreading and compaction. The present invention recognizes the use of dilute acids as leaching fluids to which pulverized DCPDH will be added, and thus teaches use of a stabilizer that is dilute acid semi-soluble.

Unlike the present invention, prior art has taught stabilization of heavy metals by addition of water soluble or water based physical encapsulation agents, and have failed to recognize the value of pulverized DCPDH which is not water soluble, yet is soluble and surface available in dilute acetic acid (TCLP), dilute sulfuric and nitric acid (SPLP/MEP) and dilute citric acid (CALWET). In particular, O'Hara (U.S. Pat. No. 4,737,356) and Forrester (U.S. Pat. Nos. 5,245,114 and 5,430,233) teach the need to add water soluble phosphates to incinerator ash, auto shredder and wire insulation wastes, and incinerator bottom ash, which are at least 5 gm/100 ml water solubility, with the preferred embodiment being 100% water soluble phosphoric acid which increases odors. Prior art stabilization methods using Portland cement, lime, cement kiln dust, phosphoric acids, and combinations also produce a

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reduced permeability matrix or solid material form by adding water (by combination or as part of the water soluble agent addition) to the stabilization recipe for a chemical reaction which presents post-stabilization handling and disposal complications, whereas the present invention use of pulverized DCPDH acts to reduce odors and metals solubility without significant reduction or increase of permeability, without formation of cement-like non-free flowing material or waste, without curing time, without water hydration and associated material and waste weigh increase, without double material and soil handling required for curing stockpiles, thus permitting immediate stabilized material or waste handling, loading, disposal or reuse and management in close proximity to residential and commercial operations. The pulverized DCPDH acid semi-soluble seed stabilization method operates on the basic principle that sufficient wet dilute acid environment contact and mixing between the material or waste and the pulverized DCPDH will occur within the TCLP, SPLP, MEP or CALWET extraction vessel. The extraction method(s) used to predict leaching potential all assume that field material or waste disposal conditions are subject to hydration by acid rainwater or acid leachate and involve some degree of interstitial mixing of heavy metals with the extract fluid over some minimal period of time in a saturated environment, and that such hydration can be simulated by an extract solute addition and mixing period. The pulverized DCPDH stabilization method thus utilizes the regulatory extraction procedure to allow for post-stabilized material or waste hydration, mixing and wet chemistry dilute acid environment contact between heavy metals and pulverized DCPDH seed. The extraction tests thus act as dilute acid stirred tank reactors, which provide the opportunity for heavy metals on the surface of materials and waste, and that which diffuses into the acid solution, to have ample opportunity to contact pulverized DCPDH seed that also has surface active and/or semi-soluble mineral formation potentials with the dilute acid soluble and/or available heavy metals. One unique benefit of the pulverized DCPDH technology is that SPLP, MEP, TCLP and CALWET extract fluid acid semi-soluble pulverized DCPDH can be applied to waste or material and dry mixed for uniformity in the field, and consequently test samples of such stabilizers are allowed to freely tumble or mix in the presence of the heavy metals in the extract solution for a given extraction period of time. This non-cemented and non-reacted acid semi-soluble pulverized DCPDH surface mixing greatly improves the wet environment substitution of heavy metals such as Pb, Cd, Cr, and Cu into DCPDH surfaces. The extraction device effectively puts the heavy metals into solution of suspension as well as acid semi-soluble pulverized DCPDH into suspension and solution and thus provides an excellent opportunity for surface substitution, sorption and precipitation of now solution soluble heavy metals. Under this chemical mechanism, some pulverized DCPDH is made available to the solution by the acid solution, and heavy metal ions are made available to the solution which in turn substitute and exchange for calcium on insoluble DCPDH surfaces and precipitate with certain semi-soluble DCPDH in the extract acid solution.

It is anticipated that pulverized DCPDH, and fine particle DCPDH to a less effective degree, can be used for both RCRA compliance actions such that generated materials from mining operations, wastewater facilities, furnaces, incinerators and other facilities do not exceed appropriate TCLP hazardous waste criteria under TCLP, or used for CERCLA (Superfund) response where stabilizers are added to waste piles or storage vessels previously generated and now regulated under RCRA as a hazardous waste pre-disposal. The preferred

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method of application of DCPDH would be in a pulverized form and in-line within the property and facility generating the heavy metal bearing material, and thus allowed under RCRA as a totally enclosed, in-tank or exempt method of TCLP stabilization without the need for a RCRA Part B hazardous waste treatment and storage facility permit(s).

DCPDH may also be used in combination with Portland cement, cement kiln dust, lime kiln dust, silicates, lime, dolomitic lime, magnesium oxide, quicklime, phosphates, lime, ferric sulfate, ferrous sulfate, ferric chloride, iron powder, iron filings, chlorides, carbonates, monoammonia phosphate (MAP), diammonium phosphate (DAP), single superphosphate (SSP), triple superphosphate (TSP), hexametaphosphate (HMP), tetrapotassium polyphosphate, dicalcium phosphate, tricalcium phosphate, monocalcium phosphate, phosphate rock, pulverized forms of all above dry phosphates, and combinations thereof depending on additional waste management needs such as strength, permeability, odor control and additional heavy metals control. In certain cases one may provide several additives such as iron, aluminum and other complexing agents which could also provide for a single-step formation of complexed apatites or low solubility minerals such as chloropyromorphite, plumbogummite or corkite. The stabilizer combination type, size, dose rate, contact duration, and application means could be engineered for each type of heavy metal bearing material or waste.

Although the exact stabilization formation molecule(s) are unknown at this time, it is expected that when heavy metals comes into contact with the pulverized DCPDH stabilizing agent in the presence of extraction fluids used during the extraction analyses, compound(s) begin to form such as a hydroxyapatites and phosphate metal precipitates through molecular substitution, aqueous precipitation, or surface sorption, which is less soluble than the heavy metal element or molecule originally in the material or waste. Specifically complexing and/or twinning of As, Hg, Pb, Cr, Cu, and Cd into pyromorphite and calcium apatites most likely occurs by adding DCPDH to the material or waste and within the extractor fluids at standard temperature and pressure. The exact odor control method is not known at this time, but is expected to result from the adsorptive nature and neutral pH range of the DCPDH. It also remains possible that modifications to temperature and pressure may accelerate of assist formation of minerals, although such methods are not considered optimal for this application given the need to limit cost and provide for optional field based stabilizing operations that would be complicated by the need for pressure and temperature control devices and vessels.

Examples of suitable stabilizing agents include, but are not limited to, DiCalcium Phosphate DiHydrate (DCPDH) in pulverized form and various fine particle form. The amounts of DCPDH agent used and the particle size selected, according to the method of invention, depend on various factors including desired solubility reduction potential, odor control desired, desired mineral toxicity, and desired mineral formation relating to toxicological and site environmental control objectives. It has been found that an amount of 0.5% pulverized DCPDH by weight of incinerator bottom ash waste, and 2.0% pulverized DCPDH by weight of combined incinerator ash, is sufficient for initial TCLP Pb and TCLP Pb and Cd stabilization to less than RCRA limits of 5.0 and 1.0 respectively and reduction of odor. However, the foregoing is not intended to preclude yet higher or lower usage of DCPDH or combinations with other agents if needed, since it has been demonstrated that amounts greater than 2% DCPDH by weight of waste also work, but are more costly. The examples

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below are merely illustrative of this invention and are not intended to limit it thereby in any way.

EXAMPLE 1

In this example refuse incinerator bottom ash was stabilized with varying amounts of phosphoric acid (75% H₃PO₄) and DCPDH with zero (0) days of sample curing pre-TCLP extraction. Both stabilized and un-stabilized ash was subsequently tested for TCLP Pb, Cd, Cr, and Cu and ash product sensible odor. Samples were extracted according to TCLP procedure set forth in Federal Register, Vol. 55, No. 126, pp. 26985-26998 (Jun. 29, 1990), which is hereby incorporated by reference. The leachate was digested prior to analysis by ICP. Phosphate mixtures produced free flowing ash suitable for land disposal, passed the paint filter test, with less than 20 PSI unconfined strength. Sample odor was tested by mixing ash with different levels of activated carbon and thereafter sensing odor by a panel of nine persons. The odor index of each sample was calculated by multiplying the average odor sense index by 33 and producing a maximum odor index of 0 to 99. The lower the number index, the stronger the odor encountered by the panel.

TABLE 1

Stabilizer Dose (%)	TCLP Cd/Pb/Cr/As (ppm)	Odor Level
0	0.148/8.03/0.23/0.005	35.3 (Baseline)
0.4% H ₃ PO ₄	0.140/0.80/0.48/0.036	31.5 (Highest Odor)
0.4% DCPDH pulverized	0.09/0.73/<0.01/<0.01	69.2 (Least Odor)

The foregoing results in Table 1 readily established the operability of the present process to dry stabilize metals thus reducing leachability and odor while also producing wastes suitable for handling and disposal without curing time. Given the effectiveness of pulverized and fine particle DCPDH in causing heavy metals to stabilize and reduce odor as presented in the Table 1, it is believed that an amount of pulverized DCPDH equivalent to less than 1% by weight of heavy metal bearing material or waste should be effective.

While this invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

I claim:

1. A method of reducing the leachability and odor of heavy metal bearing material or waste in incinerator bottom ash, comprising contacting the heavy metal bearing material or waste in the incinerator bottom ash with pulverized or fine particle DiCalcium Phosphate DiHydrate (DCPDH) in an amount effective in reducing the leaching of heavy metals from the material or waste in the incinerator bottom ash to a level no more than non-hazardous levels as determined in an EPA TCLP test, performed on the stabilized material or waste in the incinerator bottom ash, as set forth in the Federal Register, vol. 55, no. 126, pp. 26985-26998 (Jun. 20, 1990), and odor in accordance with odor index by olfactory measure.

2. The method of claim 1 wherein the incinerator bottom ash contains at least one of As, Ag, Ba, Cd, Cr, Pb, Se, Hg, Sb, Cu, Ni and Zn bearing material or waste and is contacted with the pulverized or fine particle DCPDH prior to collection of the material or waste in containers.

3. The method of claim 1 wherein the incinerator bottom ash contains at least one of As, Ag, Ba, Cd, Cr, Pb, Se, Hg, Sb,

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Cu, Ni and Zn bearing material or waste and is contacted with the pulverized or fine particle DCPDH during or after collection of the material or waste in containers or during or after generation of the material or waste as a regulated waste.

4. The method of claim 1, wherein the pulverized or fine particle DCPDH is combined with cement kiln dust, Portland cement, silicates, lime, dolomitic lime, magnesium oxide, quicklime, phosphates, lime, ferric chlorides, ferric sulfates, ferric ions, iron powder, iron filings, chlorides, carbonates, monoammonia phosphate (MAP), diammonium phosphate (DAP), single superphosphate (SSP), triple superphosphate (TSP), hexametaphosphate (HMP), tetrapotassium polyphosphate, dicalcium phosphate, tricalcium phosphate, monocalcium phosphate, phosphate rock, pulverized forms of all above dry phosphates, mineral complexing agents, or combinations thereof.

5. A method of reducing the leachability and odor of combined heavy metal bearing material or waste in incinerator bottom ash, comprising contacting the heavy metal bearing material or waste in the incinerator bottom ash with pulverized or fine particle DiCalcium Phosphate DiHydrate (DCPDH) in an amount effective in reducing the leaching of combined heavy metals from the material or waste to a level

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no more than non-hazardous or non-acceptable levels as determined in the Synthetic Precipitant Leaching Procedure (SPLP) test, Multiple Extraction Procedure (MEP) test, United Kingdom carbonated DI water leach test, Japan carbonated DI water leach test or Swiss sequential water leach test, performed on the stabilized material or waste in the incinerator bottom ash, and reducing odor to desired levels.

6. The method of claim 5 wherein the incinerator bottom ash contains at least one of As, Ag, Ba, Cd, Cr, Pb, Se, Hg, Sb, Cu, Ni, and Zn and is contacted with the pulverized or fine particle DCPDH prior to collection of the waste or materials in containers.

7. The method of claim 5 wherein the incinerator bottom ash contains at least one of As, Ag, Ba, Cd, Cr, Pb, Se, Hg, Sb, Cu, Ni, and Zn and is contacted with pulverized or fine particle DCPDH during or after collection of the waste or material in containers or during or after generation of the waste or material as a regulated waste.

8. The method of claim 1, wherein the amount of the pulverized or fine particle DCPDH contacted with the incinerator bottom ash is at least about 0.5% by weight of the incinerator bottom ash.

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